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WADC TECHNICAL REPORT 53-192
Part XIII

MECHANISM OF RAIN EROSION

Part XIII. Mechanism Studies on Neoprene Coatings

Olive G. Engel

National Bureau of Standards

JULY 1959

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PART XIII

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Part XIII. Mechanism Studies on Neoprene Coatings

Olive G. Engel

National Bureau of Standards

JULY 1959

Materials Laboratory
Contract No. AF 33(616) [illegible]3-12
Project No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the National Bureau of Standards under USAF Contract No. AF(616)-58-12. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73400, "Structural Plastics". The project was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. George P. Peterson acting as project engineer.

The experimental work that is reported was accomplished with the cooperation of the Minnesota Mining and Manufacturing Company, the Cornell Aeronautical Laboratory, the Gates Engineering Company, and the Goodyear Tire and Rubber Company.

This report covers the period of work from about October 1954 to June 1958.

ABSTRACT

The mechanism by which neoprene coatings fail is of interest because air traffic will be carried on for many years to come in the altitude range in which rain is still encountered and in the velocity range for which neoprene coatings are a solution to the rain-erosion problem. This report is an account of studies that have been made to determine the mechanism by means of which neoprene coatings eventually fail under high-speed rain impingement. Results of tests involving antiozonant applications to the neoprene coatings are encouraging enough to warrant further experiments with such applications.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

LIST OF ILLUSTRATIONS (continued)

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1. Introduction

Of the large number of hard-setting plastic coatings and of resilient rubber and synthetic rubber coatings that have been tested for rain-erosion resistance, neoprene has been found to be one of the most erosion-resistant up to impingement velocities of 500 mi/hr. Air traffic will be carried on for many years to come in the altitude range in which rain is still encountered and in the velocity range for which neoprene is a solution to the rain-erosion problem. The mechanism by which neoprene eventually does fail under waterdrop impingement is, therefore, of considerable immediate interest.

Neoprene itself does not adhere strongly to glass reinforced plastic laminates. It must be bonded to the laminate by a primer coating. The success of the neoprene topcoat in resisting high-speed rain impact depends strongly on the success of the topcoat-primer-laminate system. The rain-erosion resistance not only of the neoprene topcoat but also of the topcoat-primer-laminate system must, therefore, be assessed in evaluating neoprene as a rain-erosion resistant material.

Manuscript released by the author June 1959 for publication as a WADC Technical Report.

2. Models of a Waterdrop

Damage that is sustained by a structural material on collision with waterdrops at high speed is a direct consequence of the impact properties of a waterdrop. Under impact conditions a waterdrop behaves as though it were a sphere of ~~hard material~~; in high-speed collisions with the planar surfaces of solids it acts like an indenter to which a compressive load has been applied. Unlike a sphere of hard material, however, a colliding waterdrop retains its liquid property of flow. The radial flow of an impinging waterdrop exerts a turning moment against protrusions from the surface of the solid that are in its path and a shear stress on the surface layers of the solid around the central point of the collision. See Section 5.1.1. The Use of models to reproduce one or more of these damaging attributes of a waterdrop in high-speed collisions with solids is very informative. A model of a waterdrop might simulate its hard-sphere property or its property of radial flow, or both.

2.1 Steel Sp~~heres and~~ Deforming Lead Pellets

Steel spheres and deforming lead pellets have been used as models of waterdrops in studies of the rain-erosion damage that occurs on methyl methacrylate plastic and 1100 aluminum. On collision with these materials at relatively low velocity a steel sphere does not flow, a lead pellet flows to about twice its original diameter, and waterdrops flow to many times their original diameter. Comparison of the damage marks made by steel spheres, deforming lead pellets, and waterdrops on collision with methyl methacrylate plastic and with 1100 aluminum has proved to be of value in understanding the mechanism of failure of these materials under high-speed waterdrop impingement [1, 2, 3][a].

An attempt was made to use deforming lead pellets as a model for waterdrops colliding against neoprene-coated panels. It was found, however, that the lead pellets provided a test that was too severe for the neoprene coating that was

---

[a] Numbers in brackets refer to the literature references at the end of this report.

used (the coating was completely removed from the metal substrate) and it was concluded that a softer waterdrop model would have to be employed. It appeared that the soft gelatin closures that are used for the coloring oil of oleomargarine or even the somewhat rubbery gelatin closures that are used as capsules for medicinal oils might prove to be satisfactory waterdrop models to fire against neoprene coatings.

2.2 Oil-Filled Gelatin Capsules

The restraining gelatin closure constitutes an important point of difference between these possible two-phase models and a homogeneous liquid drop that has no restraining skin except surface tension to resist its flow. It was anticipated that this objectionable difference would be less important in the very soft gelatin closures used to contain the coloring oil for oleomargarine than in the more durable rubbery gelatin capsules used for the medicinal oils. After extensive correspondence with the Gelatin Products Division of the Scherer Corporation, however, it was found that soft gelatin closures that would be small enough to enter the barrel of the Benjamin Franklin air rifle that was to be used were not available, and that, due to production difficulties, it was doubtful whether such a closure of the required size could be manufactured.

It was decided to use gelatin capsules containing halibut oil that were found to be available on the local market and that were sufficiently small to enter the gun barrel. The undesirable characteristic of the more durable gelatin capsule of inhibiting the normal radial flow of the oil may be partly overcome by soaking the capsule in water before firing it.

The validity of using oil-filled gelatin capsules of this kind as a model for waterdrops was tested by firing them against methyl methacrylate plates of different thickness. The type of damage mark that forms on methyl methacrylate as a result of impingement with steel spheres, deforming lead pellets, and waterdrops is known [1, 2]. A high-speed moving picture was also taken of an oil-filled gelatin capsule colliding with a methyl methacrylate plate.

Damage marks that were made on 1/8-in. and on 1/4-in. Lucite sheet are shown in Figures 1 and 2. Two points of similarity between these damage marks and those that were produced on methyl methacrylate by impingement of steel spheres, deforming lead pellets, and waterdrops are that: (a) the damage mark consists of a circle of crazing and (b) the center spot of the collision, which is under compression during the collision, is undamaged. These similarities in the appearance of the damage marks indicate that the mechanism by which the marks were produced is the same.

There is no evidence of damage to the methyl methacrylate plastic as a result of the radial flow of the oil. In the case of collisions of deforming lead pellets and of waterdrops with methyl methacrylate plastic the radial flow of the projectile caused a widening of the craze cracks and a breaking out of material along the craze cracks in the direction of the flow of the projectile [1, 2].

From the high-speed moving picture of the collision of an oil-filled gelatin capsule with methyl methacrylate plastic at a velocity of about 720 ft/sec it appears that the gelatin capsule acts as an efficient restraining case for the contained oil. The gelatin capsule appears to burst during the collision at one or more of its weakest points and the oil, which must be under pressure, seems to be atomized or vaporized through the resulting holes. This behavior is altogether different from that of an impinging liquid drop.

Although the oil contained in the gelatin capsule does not undergo the radial flow that a liquid drop would undergo as a result of such a collision, the gelatin capsule does appear to simulate the hard-sphere property of an impinging liquid drop without cutting a soft rubbery coating entirely off the metal surface to which it was applied. It can be hoped that the stretch of the gelatin capsule as it flattens against the surface of the solid may exert a shear stress that will simulate the shear stress exerted by the radial flow of an impinging drop of water.

3. Response of Several Different Neoprene Based Coatings

In order to determine (a) what properties of a neoprene coating operate to establish its resistance to high-speed waterdrop impingement and (b) what properties of a neoprene

2 3

FIGURE [illegible]. DAMAGE MARKS MADE BY IMPACT OF OIL-FILLED GELATIN CAPSULES ON 1/8-IN. LUCITE SHEET

1. GELATIN CAPSULE SOAKED FOR 2 MIN; IMPACT VELOCITY 720 FT/SEC
2. GELATIN CAPSULE SOAKED FOR 2 MIN; IMPACT VELOCITY 900 FT/SEC
3. OPPOSITE SIDE OF LUCITE SHEET FOR THE DAMAGE MARK OF PICTURE 2

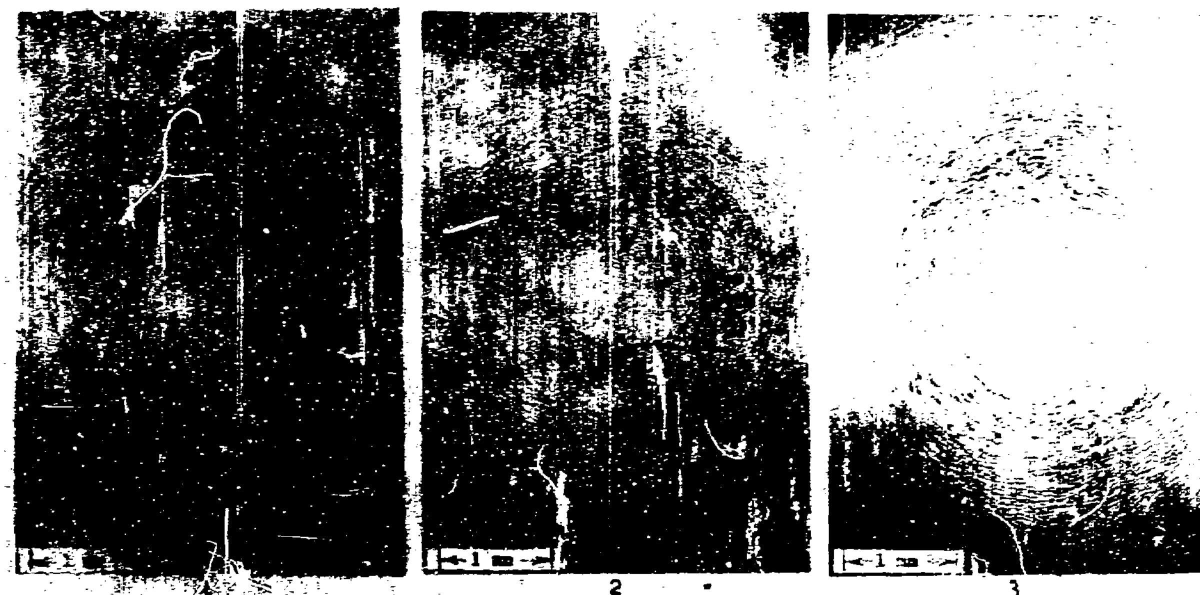


FIGURE 2 DAMAGE MARKS MADE BY IMPACT OF OIL-FILLED GELATIN CAPSULES ON 1/4-IN. LUCITE SHEET

1. GELATIN CAPSULE DRY; IMPACT VELOCITY >900 FT/SEC
2. GELATIN CAPSULE SOAKED IN WATER FOR 2 MIN; IMPACT VELOCITY 720 FT/SEC
3. GELATIN CAPSULE SOAKED IN WATER FOR 2 MIN; IMPACT VELOCITY 900 FT/SEC

coating lead to its eventual failure under high-speed waterdrop impingement, the response of several different neoprene coatings was studied. The coatings were: MMM EC-539, MMM EC-539 modified as to curing temperature and curing time (Coatings-A, -B, and -C), Gates white neoprene KV-9433, and the two neoprene coating systems that have met MIL-C-7439 requirements, Goodyear 23-56 and Gaco N-79.

3.1 MMM EC-539 Neoprene

Three 1/8-in.-thick flat panels and three 1/16-in.-thick airfoil shaped Cornell Aeronautical Laboratory rain-erosion test specimens were sent to the Minnesota Mining and Manufacturing Company to be coated with MMM EC-539 neoprene coating. The specimens were given one dip coat of EC-1022 general purpose adhesive as primer and two dip coats of EC-539 neoprene based coating. The film thickness was from 8 to 10 mils. The three flat panels were used for tests by impingement of oil-filled gelatin capsules; the three airfoil shaped specimens were sent to the Cornell Aeronautical Laboratory for test by artificial rain impingement.

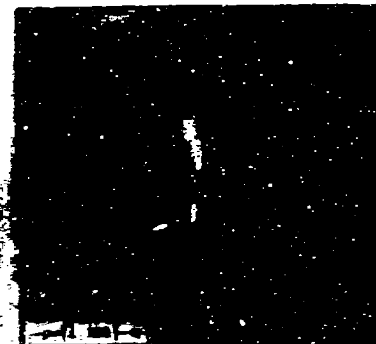
3.1.1 Damage Marks Produced on MMM EC-539 Neoprene by Impingement of Oil-Filled Gelatin Capsules

Oil-filled gelatin capsules were fired at a flat panel coated with MMM EC-539 neoprene. Each of the oil-filled gelatin capsules that was fired was soaked in water for 2 min before it was inserted in the gun barrel. The point of the gun was maintained at approximately 12 in. from the target panel for each shot. Views of the damage marks that were made by the impinging oil-filled gelatin capsules are shown in pictures 1, 2, and 3 of Figure 3.

At low magnification the damage mark that was produced at an impingement velocity of 320 ft/sec appeared to consist of a very dim, more or less circular trace. It is shown at approximately X10 magnification in picture 1 of Figure 3. When the magnification was increased the trace was seen to consist of raised edges of the coating along short irregular wrinkles or cuts.

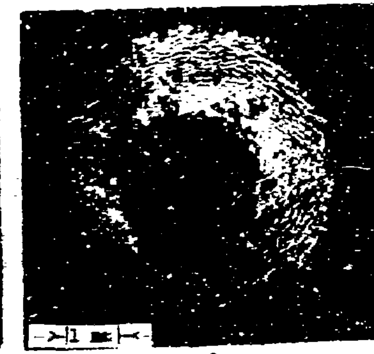
1

VELOCITY 320 FT/SEC



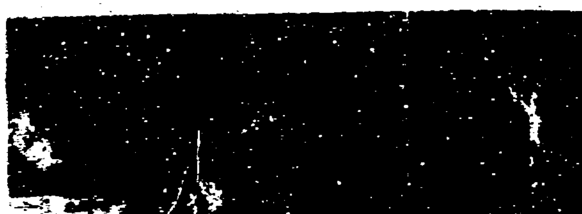
2

VELOCITY 720 FT/SEC



3

VELOCITY 900 FT/SEC



VELOCITY 880 FT/SEC

5

VELOCITY 880 FT/SEC

FIGURE 3 ABRASION OF MMM EC-539 NEOPRENE

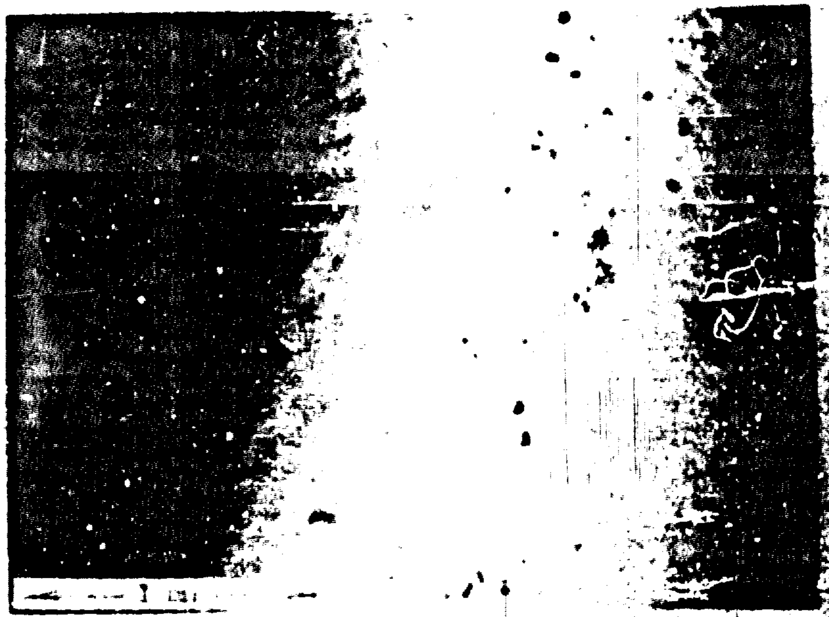
UPPER: BY IMPINGEMENT OF OIL-FILLED GELATIN CAPSULES
LOWER: BY IMPINGEMENT OF WATERDROPS

The damage mark made by an oil-filled gelatin capsule at an impingement velocity of about 720 ft/sec was similar in general appearance to that made at an impingement velocity of 320 ft/sec. However, the damage was more severe; at low magnification the circular trace appeared not only to consist of a removal of gloss but of distinct wrinkles. When the magnification was increased the damage appeared to be a coarse irregular wrinkling as though the surface skin of the coating had been given a two-dimensional stretch to the point of permanent set and then released. In some areas the wrinkling was more regular and took on the appearance of more or less parallel ridges. The edges of some of these wrinkles were so sharp that it seemed possible that they might be edges of coating that had curled or turned up along an array of cuts in the coating. Picture 2 of Figure 3 shows this damage mark at approximately X10 magnification.

The damage mark that resulted from the impact of an oil-filled gelatin capsule at an impingement velocity of about 900 ft/sec had the same general appearance as the damage marks made at the lower impingement velocities. However, the impression that the wrinkles are the rolled back edges of cuts in the coating is even stronger. Picture 3 of Figure 3 shows this damage mark at approximately X10 magnification. When this damage mark was viewed with a stereomicroscope it could be seen that it is not flat as it appears to be in the picture. The undamaged center is not depressed but the circle of wrinkles or cuts is depressed.

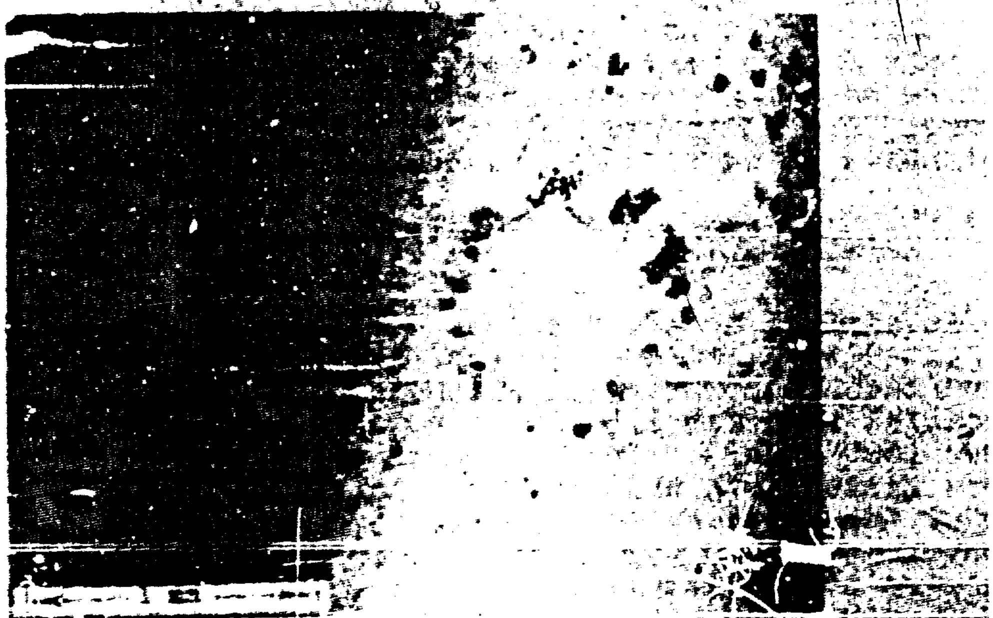
3.1.2 Damage Produced on MMM EC-539 Neoprene by Impingement of Waterdrops

An airfoil shaped specimen of 1/16-in. aluminum alloy that was coated with MMM EC-539 neoprene was tested on the Cornell Aeronautical Laboratory rotating arm tester in 1-in./hr artificial rain for 1.5 min at a relative velocity of 880 ft/sec (600 mi/hr). Inspection of this specimen showed that it was marked with what appeared to be circles of damage. Some of these are shown in pictures 4 and 5 of Figure 3. Pictures at higher magnification, in which something of the structure of the damage can be seen, are shown in Figures 4, 5, and 6. The structure of the damage of which the circles are made up strongly resembles the wrinkling or cutting of which the circles produced by the impact of the oil-filled gelatin capsules were made up. The structure



1

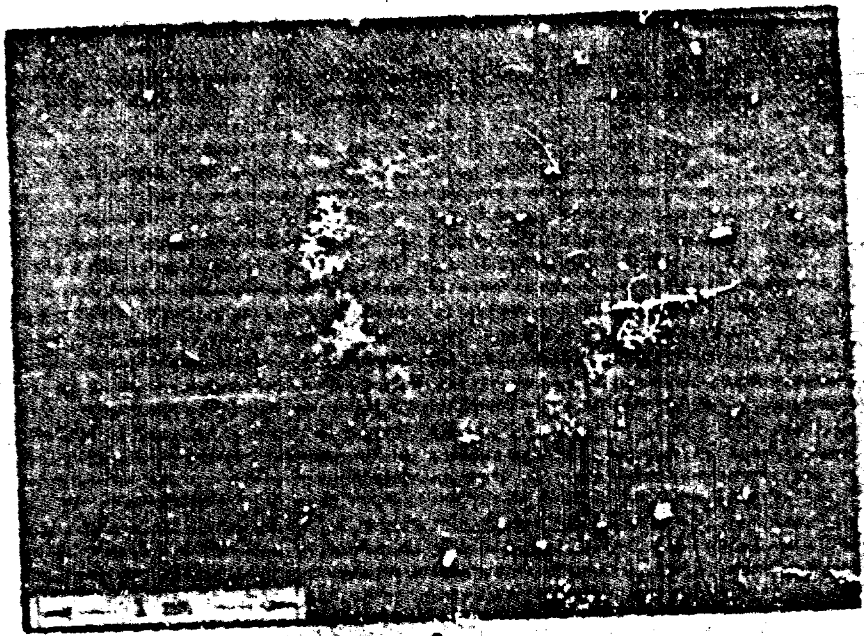
VELOCITY 880 FT/SEC



2

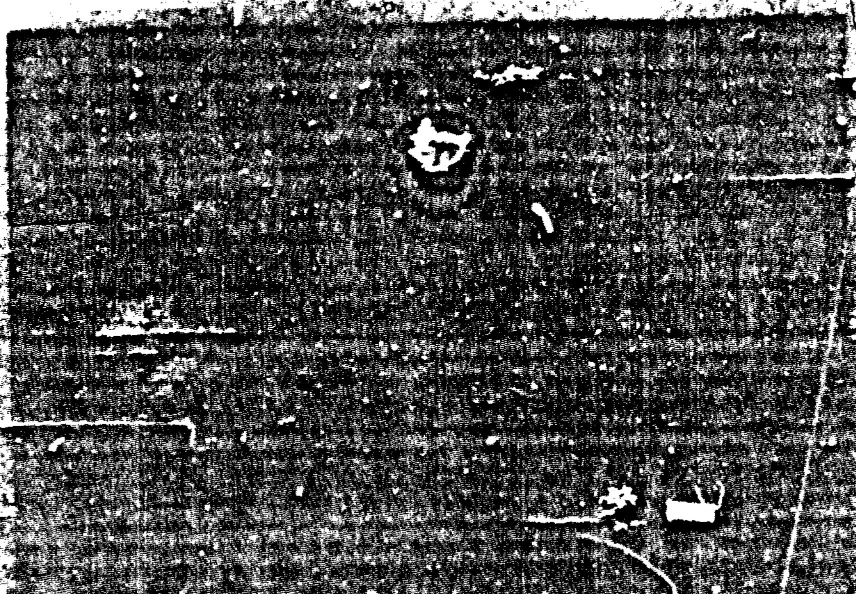
VELOCITY 980 FT/SEC

FIGURE 4 WATER DROP IMPINGEMENT ABRASION OF MMM EC-539 NEOPRENE



1

VELOCITY 880 FT/SEC



VELOCITY 880 FT/SEC

FIGURE 5 STRUCTURE OF WATERDROP IMPINGEMENT ABRASION OF MIM 8C-539 NEOPRENE

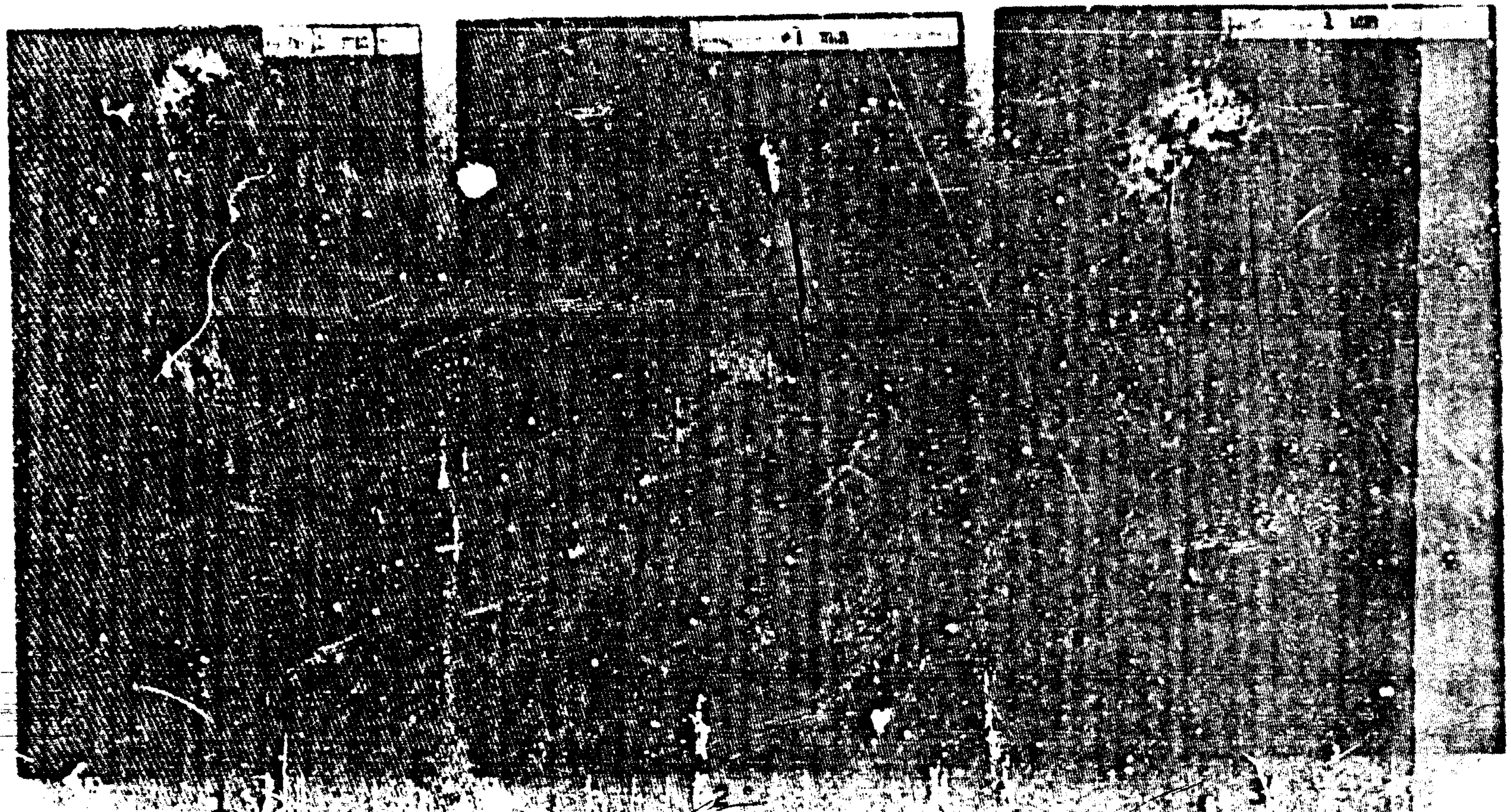


FIGURE 6 STRUCTURE OF A SINGLE DAMAGE MARK PRODUCED ON MMM EC-539 NEOPRENE BY IMPINGEMENT OF WATERDROPS AT A VELOCITY OF 980 FT/SEC

1. AT LOW MAGNIFICATION
2. WITH CAMERA FOCUSED AT LEFT EDGE OF THE MARK
3. WITH CAMERA FOCUSED AT RIGHT EDGE OF THE MARK

is similar to the abrasion pattern for rubber that has been reported by Schallamach [4, 5, 6]. See Section 4.1.

It is possible that these circles of abrasion may be caused by the radial flow of individual waterdrops after the neoprene surface has become weakened by other waterdrop blows that were not themselves able to cause visible damage. The circles are not caused by every waterdrop that impinges against the specimen because, if this were the case, there would be so many circles of abrasion after 1.5 min of test at a velocity of 600 mi/hr in 1-in./hr rain that they would overlap. If these circles are caused by the radial flow of water from single drops, the wrinkles or trenches of which they are composed should be perpendicular to radii of the flow. This may be true of the circle of abrasion in picture 1 of Figure 5, but in the circle of abrasion shown in picture 2 of Figure 5 the trenches seem all to be oriented in the same direction.

These circles of abrasion may have an entirely different origin. They may be simply raised circles in the coating that were left when bubbles in the coating opened during its cure. Any protrusion above the planar surface of the coating would be more subject to abrasion by the flow of water over the airfoil shaped specimen than the planar surface itself. On this picture of the origin of these marks it would be expected that the trenches for a given circle should have about the same orientation and that this same orientation should be seen on other less symmetrical non-circular protruding areas. Picture 1 of Figure 6 provides some evidence for this explanation of the origin of these circles of abrasion. The fact that areas exist that are not circular but that are still marked with the more or less parallel trenches is evidence in favor of this explanation.

3.2 Modified MMM EC-539 Neoprene Coatings

Flat plates and Cornell Aeronautical Laboratory rain-erosion test specimens of aluminum alloy were sent to the Minnesota Mining and Manufacturing Company to be coated with three neoprenes of different properties. The neoprene films were applied by dip coating to a dry depth of 10 mils before cure which produced a coating thickness of 8 to 10 mils after cure. The coatings that were applied are designated as Coating-A, Coating-B, and Coating-C. The difference in the properties of these coatings was produced by varying the

curing conditions of MMM EC-539 neoprene plus EC-566 accelerator. Coating-A was cured at 140°F for 72 hrs; Coating-B was cured at 210°F for 8 hrs; Coating-C was cured at 275°F for 1 hr.

The tensile strength, per cent elongation, and shear strength of the coatings that resulted from use of these curing conditions were determined by the Minnesota Mining and Manufacturing Company. A pendulum-type tensile tester was used to determine the tensile strength and the percent elongation. One-inch lap shear bonds were pulled in a pendulum machine to determine the shear strength. The lap shear bonds were prepared by sandwiching the neoprene between aluminum sheets using EC-1022 as the metal primer and curing under the specified conditions. The true shear strength of the EC-539 neoprene film was not measured because failure always occurred either at the primer-to-coating or at the primer-to-metal bond. The tensile strength, percent elongation, and shear strength (of the adhesion bond) data for a 10-mil film thickness are given in Table 1.

Table 1.

Curing Schedule and Physical Properties of Coating-A, Coating B, and Coating-C

	Curing Schedule time hr	temperature °F	Tensile Strength psi	Shear Strength+ psi	Elongation per cent
Coating-A	72	140	2,700	250	170
Coating-B	8	210	4,000	500	137
Coating-C	1	275	4,800	500	96

+ Shear strength of the adhesive bond

3.2.1 Damage Marks Produced on Modified MMM EC-539 Neoprene by Impingement of Oil-Filled Gelatin Capsules

Oil-filled gelatin capsules were fired from a Benjamin Franklin air rifle at flat plates coated with modified MMM EC-539 neoprene (Coating-A, Coating-B, and Coating-C). The plates carrying the neoprene coatings were clamped against a backing plate. The gun was held 12 in. from the neoprene coated plate and the gelatin capsules were fired at the plate at 90° incidence. The gelatin capsules were soaked in water for 2 min before the shots were made. Shots were made at velocities of approximately 320, 720, and 900 ft/sec. Microscopic inspection of the spots that were struck by the gelatin capsules provided the following information.

On Coating-A no marked damage was observed as a result of the shot made at a velocity of about 320 ft/sec. The shot made at a velocity of approximately 720 ft/sec produced a hardly discernible semicircle of what appeared to be cuts or wrinkles in the coating. The shot made at a velocity of about 900 ft/sec produced a complete circle of what appeared to be cuts or wrinkles in the coating. A view of this damage mark is shown in picture 1 of Figure 7.

On Coating-B no damage was produced by the shots that were made at the approximate velocities of 320 and 720 ft/sec. The shot made at a velocity of about 900 ft/sec produced arcs of what appeared to be cuts or wrinkles in the coating. A view of this damage mark is shown in picture 2 of Figure 7.

On Coating-C no marked damage was produced by the shot made at a velocity of about 320 ft/sec or by the shot made at a velocity of approximately 720 ft/sec. The shot made at a velocity of about 900 ft/sec produced arcs of what appeared to be cuts or wrinkles in the coating. This damage was surrounded by a large blister of coating. A view of this damage mark is shown at two magnifications in pictures 3 and 4 of Figure 7.

The section of Coating-A containing the damage mark shown in picture 1 of Figure 7 was cut loose from the aluminum plate and the circle of damage was inspected at high magnification. The circle of damage was seen to consist of raised ridges or edges of rubber. The same type of damage (raised flaps of rubber) results when a sharp pointed marking pencil or a razor blade is dragged across the neoprene surface. Such kinds of damage are shown in Figure 8. This type of damage to rubber has been discussed by Schallamach [4, 5, 6] and has been characterized as rubber abrasion. Throughout the remainder of this report this type of damage to the surface of a neoprene coating will be referred to as rubber abrasion. The way in which this abrasion is produced is discussed in Section 4.1.

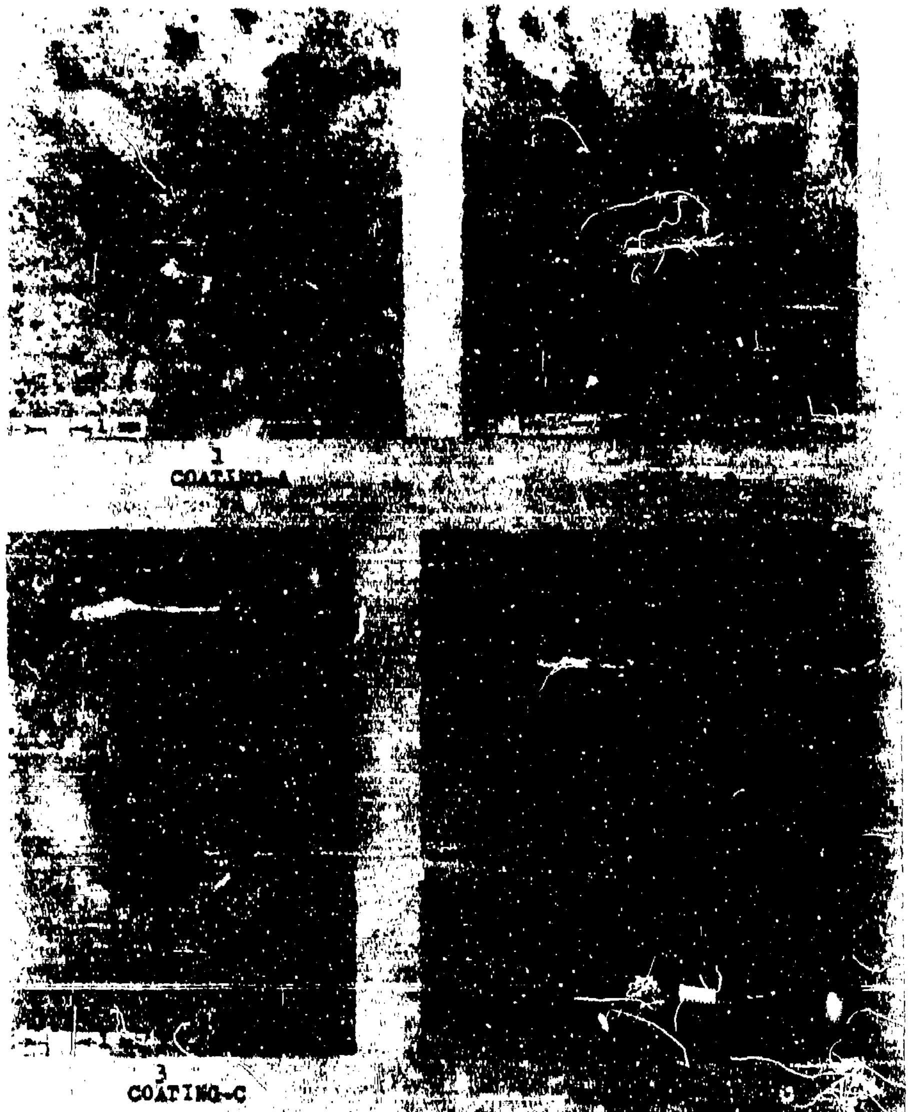
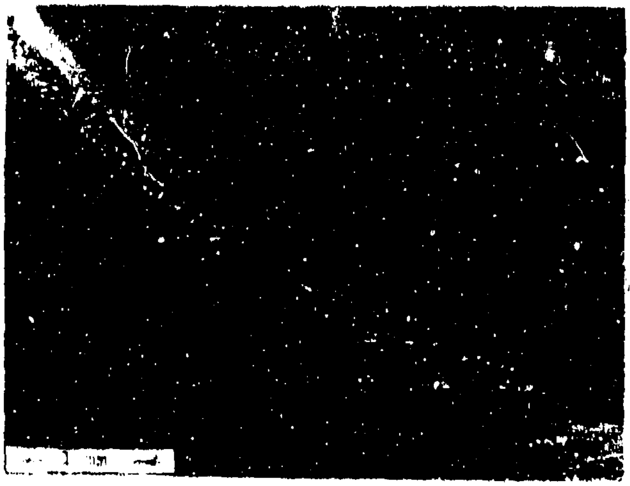


FIGURE 7 DAMAGE MARKS PRODUCED BY OIL-FILLED [illegible] COLLISION AGAINST THREE NEOPRENE COAT[illegible] PROPERTIES AT A VELOCITY OF 900 [illegible]



1

2

ABRASION BY TUNGSTEN-CARBIDE MARKING PENCIL MOVING DOWNWARD

3

ABRASION BY RAZOR EDGE MOVING FROM LEFT TO RIGHT

FIGURE 8 MECHANICAL ABRASION OF MMM EC-539 NEOPRENE

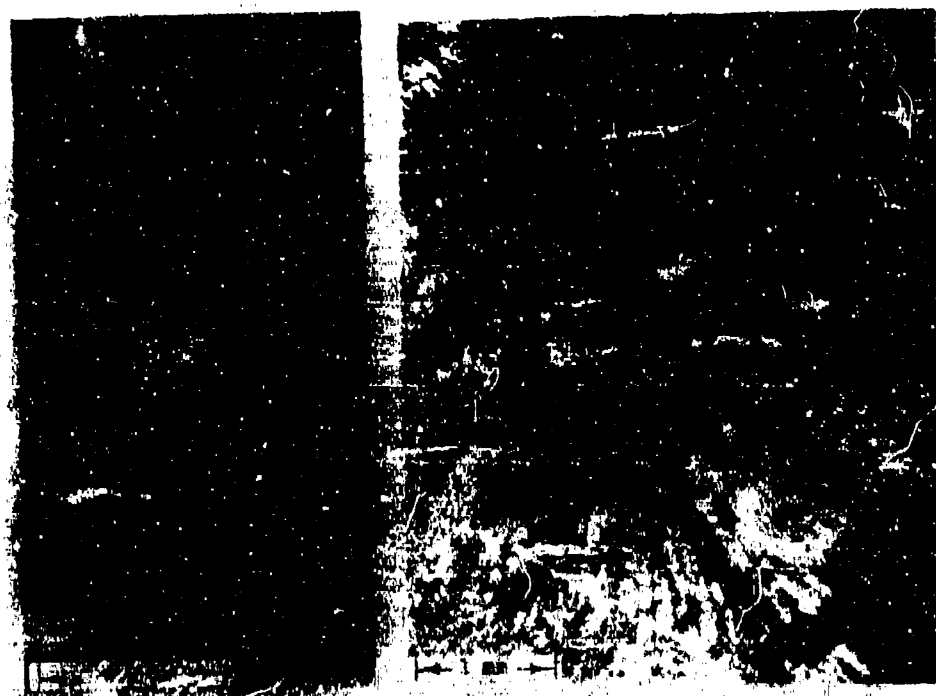
The pictures of Figure 7 show thatonly Coating-C failed due to loss of adhesion. From Table 1 it can be seen that Coating-C had the lowest percent elongation of the three coatings. If a rubber coating has a high degree of rigidity a shear stress exerted on its surface may be transmitted through it to the adhesion bond and if the stress is sufficiently great the adhesion bond may fail. The area of coating that was given a radial stretch to the point of permanent set during the collision will then be raised from the surface to which it had been bonded in the form of a coating bubble or coating blister.

It will be seen in the following sections that damage marks comparable to those shown in Figure 7 are produced on these coatings by very high-speed waterdrop impingement and that the use of oil-filled gelatin capsules as a model for waterdrops in very high speed collisions is fully justified.

3.2.2 Damage Produced on Modified MMM EC-539 Neoprene by Impingement of Waterdrops

Nine airfoil shaped rain-erosion specimens were coated with MMM EC-539 neoprene by the Minnesota Mining and Manufacturing Company. The curing schedule used for these specimens was such that three of the specimens were of Coating-A, three of the specimens were of Coating-B, and three of the specimens were of Coating-C. These specimens were tested on the Cornell Aeronautical Laboratory rotating arm tester at a velocity of 600 mi/hr in 1-in./hr artificial rain. The three specimens of each coating were tested for 25 sec, 1 min, and 2 min, respectively. The visual appearance of these specimens after test was reported. The specimens were returned to the National Bureau of Standards for study.

Examination of the specimens of Coating-A, Coating-B, and Coating-C that were tested for 25 sec, 1 min, and 2 min provided the information that the coatings on all of these specimens were characterized by irregular patches of the small more or less parallel shallow trenches of rubber abrasion. In many cases these patches were circular or consisted of arcs of circle. Picture 1 of Figure 9 is a view at high magnification that shows the parallel-trench structure; this picture was taken on a specimen of Coating-C. It is difficult to take pictures at high magnification on the rain-erosion test specimens because of their curvature.



1 2

FIGURE 5 VIEWS OF WATERDROP IMPINGEMENT DAMAGE ON COATING-C

The quantity of these patches of abrasion increased in amount as the test time for the coatings varied from 25 sec to 2 min. There seemed to be as much or more of this rubber abrasion within any given period of test in the order of Coating-A least to Coating-C most. In addition to being beset with the rubber abrasion, the specimen of Coating-B that was tested for 2 min had lost adhesion on the high-speed end with formation of bubbling; it had also torn open there.

The waterflow from intercepted drops follows curved trajectories on the airfoil shaped specimens; the flow runs off on both sides of the leading edge. The curved trajectories were clearly marked by the more or less parallel trench structure of rubber abrasion on the specimens of Coating-A, Coating-B, and Coating-C that were tested for 2 min. Picture 2 of Figure 9 is a view of these curved trajectories on Coating-C; the leading edge of the specimen is on the diagonal from upper left to lower right in the picture. The circular nature of many of the patches of rubber abrasion can be seen in this picture.

The evidence that has been presented appears to indicate that the damage that increases with time on this particular neoprene coating system for the test velocity and rain density that were used is the rubber abrasion which appears to be progressing to a point at which it will cover the entire leading edge of the specimen. The percent elongation of these coatings is in the order of Coating-A most to Coating-C least; the development of rubber abrasion on the surface of the neoprene appeared to be in the order of Coating-A least to Coating-C most. From this evidence it would appear that a neoprene coating having a high elongation property should be more rain-erosion resistant than a neoprene coating having a low elongation property. Coating-A had the lowest tensile strength of the three coatings. This, however, does not mean that tensile strength is not an important property in a rain-erosion resistant coating. A minimum tensile strength is necessary and it is possible that if Coating-A had had a higher tensile strength it would have been more erosion resistant.

3.2.3 Resistance of Modified MMM EC-539 Neoprene to Very High Speed Waterdrop Impingement

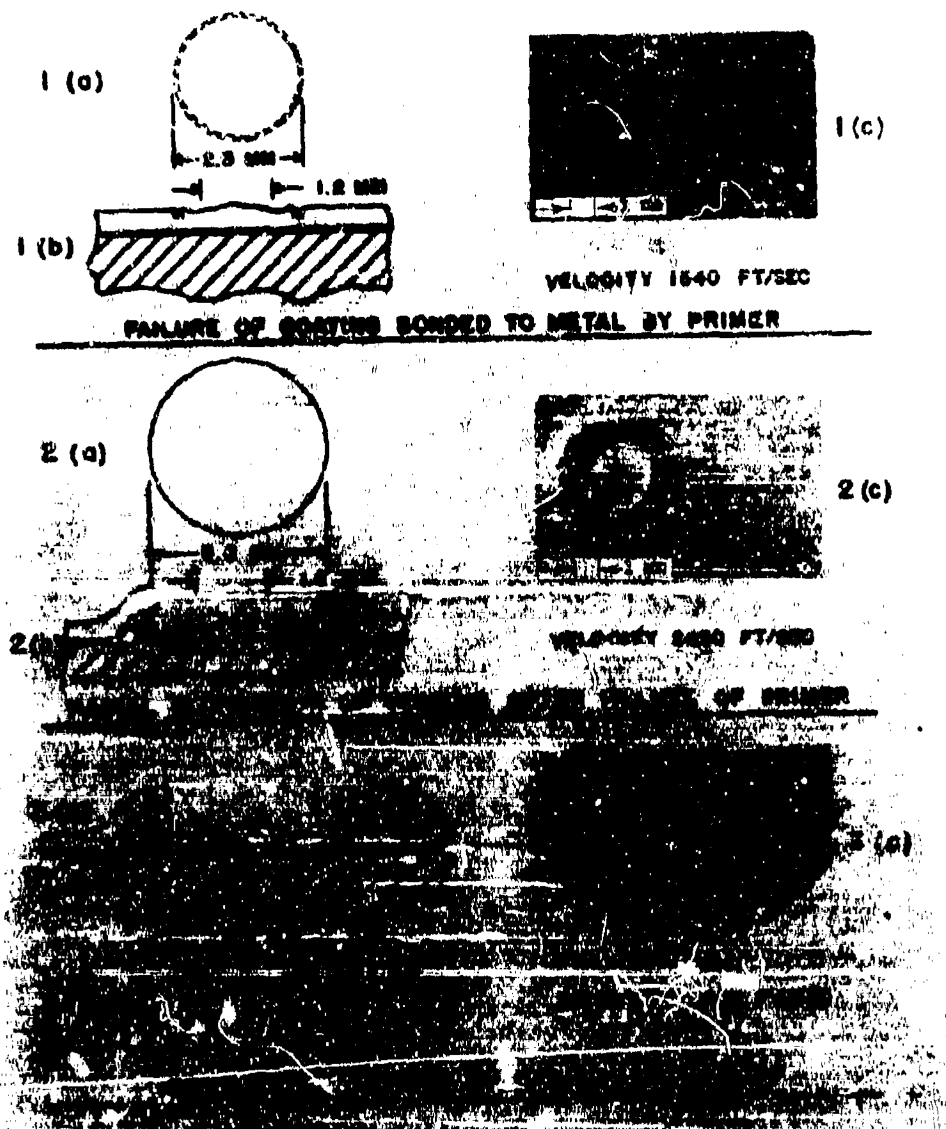
Specimens for use in waterdrop impingement tests at very high velocity were coated with MMM EC-539 neoprene by the Minnesota Mining and Manufacturing Company. The curing schedules that were used produced Coating-A, Coating B, and Coating-C on the surfaces

to which the MMM EC-539 neoprene was applied. These specimens were sent to Convair where very high velocity impingement tests were carried out.

The damage marks made by approximately 2-mm waterdrops on Coating-A at an impingement velocity of 1,540 ft/sec are shown in picture 1 (c) of Figure 10. Dimensions of the damage mark closest to the edge of the specimen are shown in sketches 1(a) and 1(b) at the left of the picture. The damage mark consists of a circular depression bounded by a circle of cutting. See cross section in sketch 1(b). The circular depression marks the region of maximum pressure exerted by the colliding waterdrop. The bottom of the circular trough is roughly half a radius from the stagnation point (center of the collision). The diameter of the circle of cutting is approximately the same as the diameter of the waterdrop that produced the damage mark. In general, the damage mark is similar to that produced by impigement of an oil-filled gelatin capsule at a velocity of about 900 ft/sec. See picture 1 of Figure 7.

There are two possible ways in which the circle of cutting may be produced. (a) Because the coating suffers severe compression, a shallow disk-shaped cavity may form in it. If this happens, strong tensile stresses will exist in the sharp knee of coating at the periphery of the cavity. These tensile stresses may be responsible for the circle of cutting. However, the high percent elongation of Coating-A makes this explanation seem unlikely. It should be possible to bend this coating into a very sharp knee without producing cuts. (b) A second explanation is that the circle of cutting is produced by the shear stress exerted by the radial flow of water from the drop during the collision. On this explanation the circle of cutting is severe rubber abrasion. Inspection of the structure of the circle of cutting with a stereoscopic microscope showed that the structure of it is completely comparable with that of rubber abrasion.

The damage mark produced at an impingement velocity of 2,480 ft/sec is shown in picture 2(c) of Figure 10. This damage mark consists of a central mound in the coating surrounded by a circular fold of coating. Dimensions of the damage mark are shown in sketches 2(a) and 2(b) at the left of the picture.


1 (a)
2.3 MM
1.2 MM
1 (b)
1 (c)
VELOCITY 1640 FT/SEC
FAILURE OF COATING BONDED TO METAL BY PRIMER
2 (a)
2 (c)
2 (b)

... FAILURE OF ...

It can be seen that the diameter of the circular fold of coating is much larger than the diameter of the circle of cutting (rubber abrasion) seen in picture 1(c). Inspection of this damage mark with a stereoscopic microscope revealed that the circle of cutting exists at the base of the fold of coating and is concealed by the overhang of the fold itself. Although the radius of curvature of the fold is very small there are no cuts in the coating along the top of the fold.

It would appear that the first stage in the formation of this damage mark was the same as that shown in picture 1(c). The shear stress exerted by the radial flow of water from the drop was apparently great enough to break the primer bond and move the coating out into a radial stretch that was severe enough to induce permanent set. The fact that there are no cuts in the acute bending of this fold of coating is evidence that the circle of cutting shown in picture 1(c) is rubber abrasion and is not the result of a tensile failure at the periphery of a disk-shaped depression.

The damage mark that was produced at an impingement velocity of 2,588 ft/sec is shown in picture 3(c) of Figure 10. It consists of a circular spot of primer surrounded by a circular area of bare metal. Beyond this is a region over which the coating has been stripped from the primer. Dimensions of the damage mark are shown in sketches 3(a) and 3(b) to the left of the picture. From a comparison of the dimensions shown in sketches 2(a), 2(b), and 3(b) it appears that the diameter of the circular spot of primer in picture 3(c) corresponds to the diameter of the central raised mound in picture 2(c) and that the outside diameter of the circle of bare metal in picture 3(c) corresponds to the diameter of the fold of coating in picture 2(c). It would appear that in the formation of this damage mark the stages shown in pictures 1(c) and 2(c) are reenacted. At this higher impingement velocity it appears that the turning moment exerted by the radial flow of water from the colliding drop is strong enough to break through the circle of cutting (rubber abrasion) at the base of the fold of coating and to rip the coating off the primer. The mechanism by which this may be accomplished is shown schematically in Figure 3(a).

The behavior that is observed for Coating-A in this very high velocity waterdrop impingement is in agreement with its property of high elongation. It would appear that whereas the high elongation property of Coating-A was desirable at an impingement

velocity of 880 ~~ft/sec~~ (600 mi/hr) in that it seemed to retard a gradual rubber abrasion, the property is undesirable when the impingement velocity is increased by a factor of three.

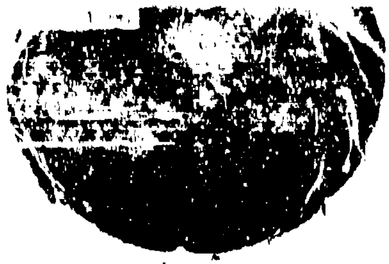
Damage marks produced on Coating-B at four different velocities are shown in Figure 11 and damage marks produced on Coating-C at two different velocities are shown in Figure 12. The damage marks shown in picture 1(c) of Figure 10, picture 1 of Figure 11 and picture 1 of Figure 12 were all made at an impingement velocity of approximately 1,520 ft/sec. Each of these damage marks consists of a circle of severe rubber abrasion. Comparison of them indicates that there are minor differences in the response of the three coatings at this velocity, however. In the case of the damage mark on Coating-A there is a circular trench or depression within the circle of cutting or rubber abrasion; in the case of Coating-B and of Coating-C this circular depression is essentially absent. This observation would seem to indicate that Coating-A is more subject to being deformed beyond its ability to recover than is Coating-B or Coating-C. The circle of rubber abrasion in these damage marks is wider for Coating-B and for Coating-C than for Coating-A. This may indicate a greater susceptibility toward abrasion in Coating-B and Coating-C than in Coating-A.

The damage marks shown in picture 2(c) of figure 10 and picture 2 of figure 12 were made at almost the same impingement velocity. These damage marks are quite different in appearance and are in agreement with the high percent elongation property of Coating-A and the low percent elongation property of Coating-C.

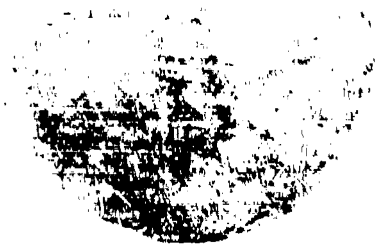
The damage mark shown in picture 3(c) of Figure 10 was made at almost the same impingement velocity as those shown in picture 4 of Figure 11. Although the damage mark made on Coating-A appears to be the most severe the coating in the vicinity of the crack on Coating-B is loosened from the primer and, probably, had the impingement velocity been a little higher, it would have been torn loose to produce a damage mark comparable to that on Coating-A. However, this has not occurred at the velocity at which the damage mark was made and it may be concluded that Coating-B is more resistant to waterdrop impingement at a velocity of about 2,600 ft/sec than is Coating-A.

3.3 Gates White Neoprene and the Standard Neoprene Coatings

Four airfoil specimens and two flat panels were coated at the Gates Engineering Company with Gaco N-79 tan neoprene and with Gates AV-[illegible] white neoprene, respectively. The Gaco N-79

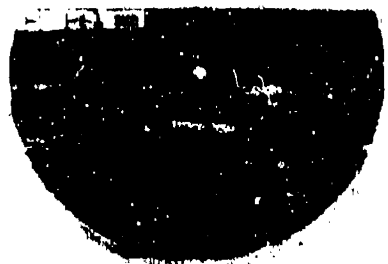


1
VELOCITY [illegible] FT/SEC



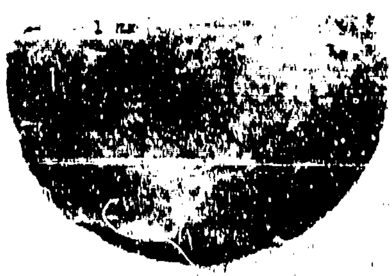
2
VELOCITY 2025 FT/SEC

3
VELOCITY 2250 FT/SEC



4
VELOCITY 2605 FT/SEC

FIGURE 11 WATERDROP-IMPACT FAILURE OF COATING-B



1
VELOCITY 1510 FT/SEC

2
VELOCITY 2475 FT/SEC

FIGURE 12 WATERDROP-IMPACT FAILURE OF COATING-C

tan neoprene was applied over Gaco N-15 isocyanate primer. The Gates KV-9433 white neoprene was applied over KV-8600 tie-cement and KV-8582 primer. Similar specimens were coated at the Cornell Aeronautical Laboratory with Goodyear 23-56 neoprene over Bostik 1007 primer. Physical properties of these coating systems are given in Table 2.

The airfoil specimens coated with each of the three neoprene coating systems were tested for rain erosion resistance at the Cornell Aeronautical Laboratory. The flat panels were used for tests of the resistance of these coating systems to impingement by oil-filled gelatin capsules and by deforming lead pellets.

Table 2

Physical Properties of Gates White Neoprene and the Standard Neoprene Coatings

Coating System			Physical Properties		
Topcoat	Primer	Tie Cement	Tensile Strength psi	Peel-Pull Adhesion lb/in.width	Elongation at Break %
Gaco N-79	Gaco N-15	----	2,020	25-40	750
Gates-White KV-9433	Gates KV-8582	Gates KV-8600	3,026	42-48	863
Goodyear 23-56	Bostik 1007	----			

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3.3.1 Damage Marks Produced on Gates White Neoprene and the Standard Neoprene Coatings by Impingement of Oil-Filled Gelatin Capsules and of Deforming Lead Pellets

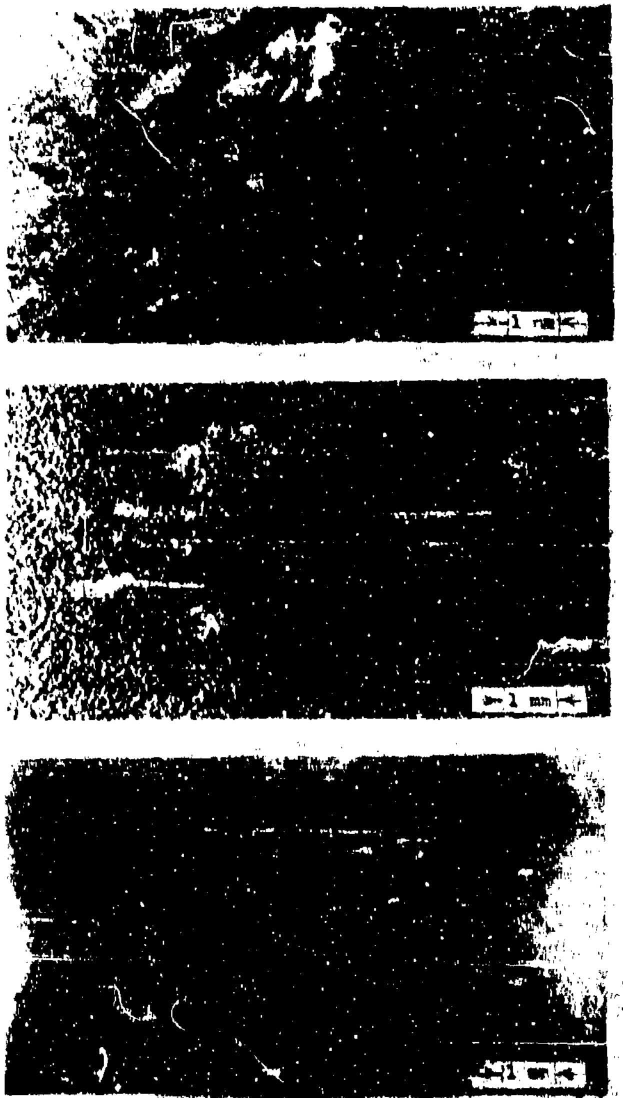
The oil-filled gelatin capsules that were used for the shots were soaked in water for 2 min. They were fired at the coated panels from a Benjamin Franklin air rifle. The distance from the muzzle of the gun to the target coating was 2 ft. The capsules were fired at velocities of 320, 720, 870, and 900 ft/sec.

Inspection at low power with a stereoscopic microscopic showed that very little damage was done to any of the coated panels by impingement of the oil-filled gelatin capsule at velocities under 900 ft/sec. Evidence of loss of adhesion could be seen in the white neoprene at an impingement velocity of 870 ft/sec and evidence of a circle of abrasion could be seen in the Gaco N-79 neoprene at this impingement velocity. Magnified views of the marks produced on the three coatings at an impingement velocity of 900 ft/sec are shown in Figure 13.

The Gaco N-79 coating appeared to be the least affected. A circular dent in the coating was observed. The Goodyear 23-56 neoprene coating was abraded around the central point of impact possibly due to the scraping of the capsule as it spread radially on the surface during the collision. The Gates KV-9433 white neoprene coating failed in adhesion and bubbled or lifted around the central point of the collision; it appears also to have suffered some abrasion.

Deforming lead pellets, which flow when they collide with a solid surface at high velocity, were also fired at the neoprene-coated panels. The pellets were fired from the Benjamin Franklin air rifle; the pellet velocities were 490, 530, and 640 ft/sec.

Magnified views of the damage marks produced on the three neoprene coatings at a pellet velocity of 490 ft/sec are shown in Figure 14. In each case a circular collar or bubble of coating was raised about the central point of the collision. The Gaco N-79 Neoprene coating appeared to suffer the least damage in that the cut in the coating was a semi-circle rather than a complete



GOODYEAR 23-56
STANDARD NEOPRENE

GACO N-79
STANDARD NEOPRENE

GATES KV-9433
WHITE NEOPRENE

FIGURE 13 RESPONSE OF THREE NEOPRENE COATINGS TO IMPINGEMENT WITH AN OIL-FILLED GELATIN CAPSULE AT A VELOCITY OF 900 FT/SEC

[illegible] 23-56 NEOPRENE

BOSTIK 1007 PRIMER

GATES KV-9433 WHITE NEOPRENE

GATES KV-8600 TIE CEMENT

GATES KV-8582 PRIMER

[illegible] OF [illegible] NEOPRENE COATINGS TO IMPINGEMENT WITH DEFORMING LEAD PELLETS AT [illegible] VELOCITY OF 490 FT/SEC

circle. The circular patch of coating at the center of the damage mark was cut completely free of the remainder of the coating in the case of the Goodyear 23-56 neoprene and in the case of the Gates KV-9433 white neoprene. The white neoprene appeared to suffer the most extensive damage; a section of the coating was torn open. Through the open hole in the white neoprene coating it appeared that the adhesion failure was between the neoprene and the underlying coats (tie-cement and primer).

Views at about 2X magnification of the damage marks that were produced on the three coatings at pellet velocities of 530 and 640 ft/sec are shown in Figure 15. The Gaco N-79 neoprene appeared to suffer the least damage and the Gates KV-9433 white neoprene appeared to suffer the most extensive damage.

At a velocity of 530 ft/sec the raised collar or bubble of coating in the Gaco N-79 neoprene was of about the same diameter as that produced in it at a velocity of 490 ft/sec but the cut in the coating was a complete circle. The raised section of coating in the Goodyear 23-56 neoprene was nearly twice as large as that produced in Gaco N-79 neoprene at this velocity. This may indicate that the adhesion bonds between the metal and primer and/or between the primer and topcoat of the Goodyear-23-56-Bostik-1007 system are weaker than those of the Gaco-N-79-Gaco-N-15 system. The adhesion failure of the Goodyear coating system appeared to be between the primer and the metal. The raised section of coating in the Gates KV-9433 white neoprene was more than four times larger than that which formed in Gaco N-79 neoprene at this velocity. There was no tearing of the white neoprene topcoat at the periphery of the coating bubble but this did occur in the case of Goodyear 23-56 neoprene. This may indicate either that the adhesion bonds of the white neoprene system are weaker than those of the Goodyear-23-56-Bostik-1007 system and permit the growth of a large bubble without undue stress to the topcoat or that the white neoprene topcoat has higher strength properties than the Goodyear 23-56 neoprene topcoat permitting the growth of a large bubble in spite of strong adhesion bonds.

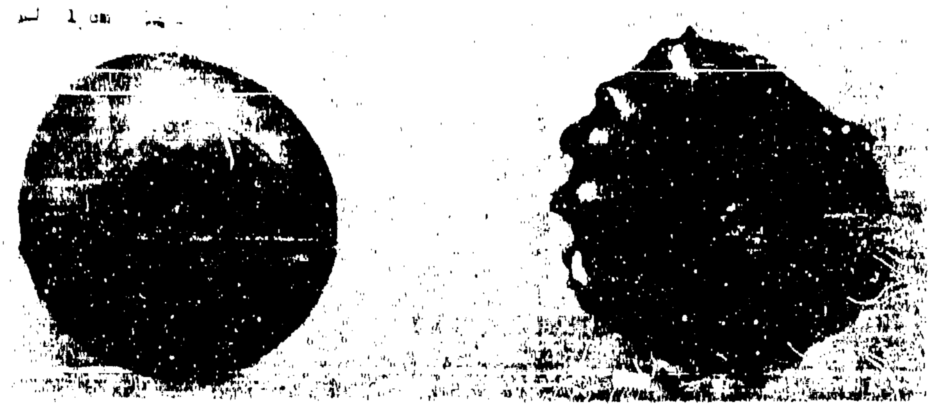
At a velocity of 640 ft/sec there is no tearing of the Gaco N-79 neoprene at the periphery of the coating bubble but such tearing did occur both in the Goodyear 23-56 neoprene and in the Gates KV-9433 white neoprene. There is some abrasion of the neoprene surface around the circular cut in the coating in the case of the white neoprene and rather extensive abrasion in the

IMPINGEMENT VELOCITY 530 FT/SEC   IMPINGEMENT VELOCITY 640 FT/SEC

GACO N-79 NEOPRENE, GACO N-15 PRIMER

IMPINGEMENT VELOCITY 530 FT/SEC   IMPINGEMENT VELOCITY 640 FT/SEC

GOODYEAR 23-56 NEOPRENE, BOSTIK 1007 PRIMER



IMPINGEMENT VELOCITY 530 FT/SEC   IMPINGEMENT VELOCITY 640 FT/SEC

GATES KV-9433 WHITE NEOPRENE, GATES KV-8600 TIE CEMENT, GATES KV-8582 PRIMER

FIGURE 15 RESPONSE OF THREE NEOPRENE COATINGS TO IMPINGEMENT WITH DEFORMING LEAD PELLETS

case of the Goodyear 23-56 neoprene, but no abrasion in the case of the Gaco N-79 neoprene.

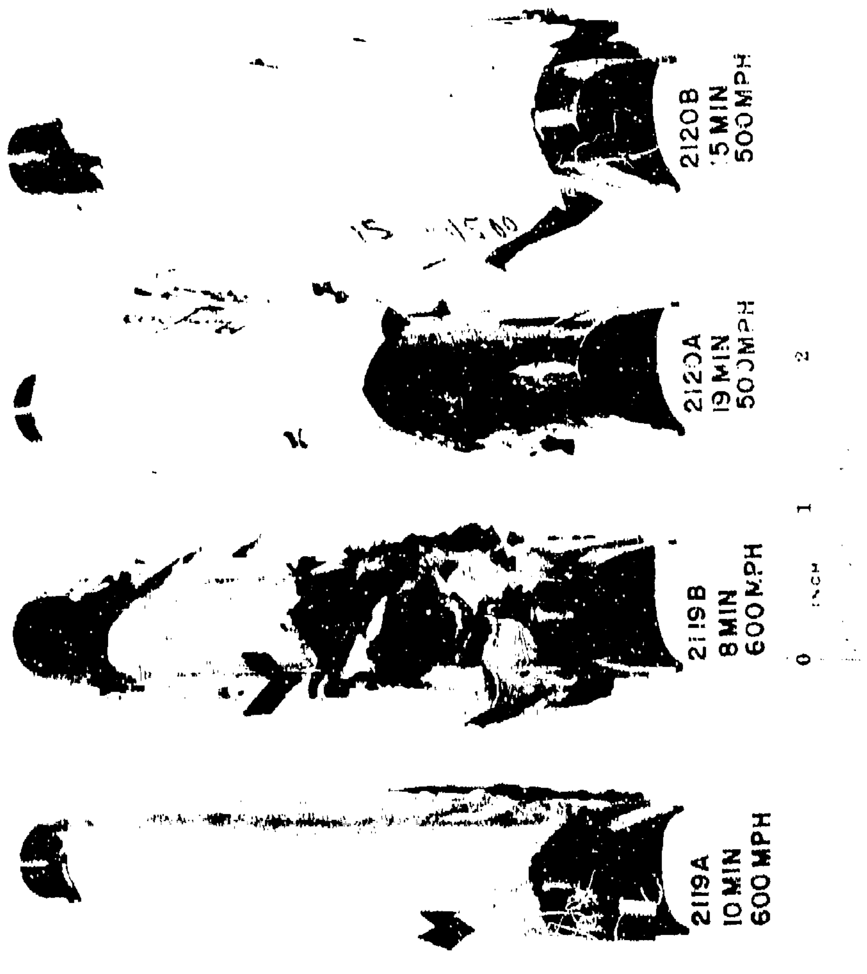
Oil-filled gelatin capsules and deforming lead pellets when they collide with a solid surface simulate the damaging properties of a waterdrop when it collides with and flows on the surface of a solid. The two damage tools that are active in a colliding waterdrop are the localized impact pressure and the radial flow of the substance of the drop with the concomitant stresses that are introduced by each. The damage produced on the three neoprene coatings by impingement of oil-filled gelatin capsules and of deforming lead pellets suggests some trends that may be looked for in the rain erosion response of these coatings. With regard to adhesion it can be expected that the white neoprene may fail extensively, the Goodyear 23-56 neoprene may fail moderately, and the Gaco N-79 neoprene may show little, if any, failure of this kind. With regard to abrasion it can be expected that the white neoprene may abrade slightly, the Goodyear 23-56 neoprene may abrade to a considerable extent, and the Gaco N-79 neoprene may suffer little or no abrasion. With regard to tearing failure it can be expected that the white neoprene may be somewhat susceptible, the Goodyear 23-56 may be the most susceptible of the three, and the Gaco N-79 may be the least susceptible of the three. The extend to which these predictions are fulfilled can be seen in the observations recorded in the following section.

3.3.2 Damage Produced on Gates White Neoprene and the Standard Neoprene Coatings by Impingement of Waterdrops

Rain-erosion test of the airfoil specimens that were coated with the three neoprene systems were made on the rotating arm at the Cornell Aeronautical Laboratory. Test of the specimens was to have been made at a velocity of 600 mi/hr in 1-in./hr rain for periods of 10, 20, 40, and 60 min. Failure of the white neoprene coating was so rapid, however, that two of the specimens that were coated with white neoprene were tested at a velocity of 500 mi/hr.

3.3.2.1 Gates KV-9433 White Neoprene

The specimens that were coated with white neoprene were numbered 2119 A and B and 2120 A and B. A picture of the four eroded specimens is shown in Figure 16. Only one specimen was tested at a velocity, in a rain density, and for a time interval comparable with that used for the other neoprene coating


2119A
10 MIN
600 MPH
2119B
8 MIN
600 MPH
0
INCH
1
2
2120A
19 MIN
500 MPH
2120B
15 MIN
500 MPH

systems. This was specimen 2119 A which was tested at a velocity of 600 mi/hr in 1-in/hr rain for 10 min. The coating on this specimen failed drastically in adhesion between the primer and the metal specimen-base. The coating loosened to form a large bubble that covered about three-fourths of the leading edge. Inspection of the eroded coating on this specimen with a stereoscopic microscope at a magnification of X20 revealed an indistinct chevron pattern in the neoprene at the low-speed end of the specimen and some abrasion of the coating surface on the leading edge. There were also randomly spaced gouges in the coating along the leading edge from about the center of the specimen to the high-speed end. The damage done to this specimen was obvious to the unaided eye whereas the specimens coated with the Gaco N-79-Gaco-N-15 and with the Goodyear-23-56-Bostik-1007 systems that were tested under the same conditions appeared to be undamaged to this degree of inspection.

3.3.2.2 Goodyear 23-56 Neoprene over Bostik 1007 Primer

The specimens that were coated with the Goodyear 23-56 neoprene over Bostik 1007 primer were numbered 2123 A and B and 2124 A and B. A picture of the eroded specimens is shown in Figure 17. Specimen 2123 A was tested for 10 min at a velocity of 600 mi/hr in 1-in./hr rain. Inspection of this specimen with a stereoscopic microscope revealed a scattering of small round holes in the coating down the leading edge. Evidence of the formation of a chevron pattern in the neoprene was observed at the low-speed end of the specimen. A crack in the coating could be seen at about the center of the leading edge.

Specimen 2123 B was tested for 20 min under the same conditions of velocity and rain rate. Microscopic inspection of this specimen also revealed a scattering of small round holes in the coating down the leading edge. The chevron pattern in the neoprene at the low-speed end of the specimen was more distinct. There was a coating bubble at about the center of the leading edge and a humpy structure at the high-speed end indicating loss of adhesion. There was some abrasion or tearing away of the surface layer especially at the high-speed end. There were also some sutures or cracks in the coating mainly at the high-speed end of the specimen.

Specimen 2124 A was tested for 40 min under the same conditions of velocity and rain rate. Microscopic inspection of this specimen again revealed a scattering of small round holes down the leading edge. The chevron pattern in the neoprene at the low-speed end

FIGURE 27. ERODED SPECIMENS THAT WERE COATED WITH GOODYEAR 23-56 [illegible]

was distinct. There was strong bubbling or lifting of the coating along the leading edge indicating loss of adhesion, and there was abrasion by scuffing up of the surface layer especially at the high-speed end. There were also some sutures or cracks in the coating.

Specimen 2124 B was tested for 60 min under the same conditions of velocity and rain rate. Inspection of this specimen with the microscope revealed a strong chevron pattern in the neoprene at the low-speed end of the specimen. The coating on this specimen was torn open down most of the leading edge. There was a strong abrasion of the surface layers and a grainy structure at the high-speed end of the specimen.

Some additional data are available for the progress of erosion on Goodyear 23-56 neoprene. Six epoxy laminate airfoil shaped specimens were coated with Bostik 1007 primer and with Goodyear 23-56 neoprene at the Cornell Aeronautical Laboratory to be tested along with some nylon specimens for the purpose of comparison. The specimens were numbered 2152B through 2157B, inclusive. The coating system was 12 mils thick. Rain erosion tests were conducted at a velocity of 500 mi/hr in 1-in./hr artificial rain for time intervals of 8, 10, 30, 35, 40, and 100 min.

Microscopic inspection of specimen 2152B that was tested for 8 min showed the presence of sutures or short cracks or cuts at the high-speed end of the specimen. There was also a background of patchy or spotty removal of a thin surface layer of coating on this part of the specimen. In the center of the specimen the surface gloss was removed from protrusions.

Inspection of specimen 2153B that was tested for 10 min showed a strong general abrasion of the surface at the high-speed end; a thin surface layer of coating was removed. There were a few broken out spots in the remaining dull surface. In the central area of the leading edge there were only closely spaced areas in which a thin layer of coating had been removed. This provides a clue as to how the total removal of the surface layer at the high-speed end of the specimen was accomplished. It appeared as though material had been scraped, torn, or peeled from the surface in many closely spaced spots. Close to the low-speed end

of the specimen there were only islands of etching in an unetched surface. At the low-speed end of the specimen the surface was essentially unetched and only isolated patches of etching existed. Tilting of the specimen to view the area slightly off the leading edge showed that there was poor mechanical coverage of the glass fabric with the neoprene; cutting failure was evident in the areas between the woven glass fibers.

Inspection of specimen 2154B that was tested for 30 min showed that a ~~complete~~ surface layer had been uniformly removed from the high-speed end. Many small cracks or sutures existed that could be a general deterioration of the coating by attack of ozone of of hydroxyl ions. At the center and at the low-speed end of this specimen the surface layer was simply removed.

Inspection of specimen 2155B that was tested for 35 min showed that the surface layer had been completely removed from the high-speed end of the specimen. Several very deep holes and many of the sutures could be seen in this part of the specimen. The etching away of the surface layer extended completely to the low-speed end. In the center of the leading edge the coating was rolling in appearance indicating possible loss of adhesion and there were occasional bro~~ken out~~ spots. At the low-speed end of the specimen the coating also had a rolling appearance. There were several pits that appeared to have been formed by bubbles that opened in the coating: these pits did not seem to be nuclei for more severe erosion.

Inspection of specimen 2156B that was tested for 40 min showed that the high-speed end was strongly abraded and was alligatored with sutures to a degree that might be referred to as a rotting of the surface layers by cracking. See Figure 18. It appeared that the sutures eventually circumscribed hunks of coating which then broke away. In the central part of the leading edge the sutures were broad and shallow and there were broken out spots. At the low-speed end of the specimen there were shallow broken out spots with evidence of small cracks or sutures. There were also spherical pits that may have formed when bubbles opened in the coating but again these did not appear to have grown into damage centers.

Visual inspection of specimen 2157B that was tested for 100 min showed two areas in which the coating was torn away down to the laminate. Microscopic inspection showed severe loss of material between sutures at the high-speed end of the specimen; deep cracks or sutures existed in the coating. See Figure 18. In the center of the leading edge there were isolated areas containing sutures and isolated broken out spots existed; there were several deep broken out spots. At the low-speed end of the specimen there was complete removal of the surface layer, general shallow erosion, and evidence of formation of shallow sutures.

The erosion that was produced on Goodyear 23-56-Bostik 1007 neoprene coated specimens at a velocity of 500 mi/hr is remarkably different from that produced at a velocity of 600 mi/hr. At a velocity of 500 mi/hr the erosion appears to consist of a general mechanical abrasion accompanied by a crack formation that could be due to attack of the neoprene by ozone or by hydroxyl ion. See Section 4.2. At a velocity of 500 mi/hr the crack formation appears to be the factor that contributes most toward eventual drastic failure of the coating. Blemishes such as bubbles that may have opened in the coating during cure do not appear to be nuclei for erosion attack. This is evidence that holes in the surface of a neoprene coating do not lead to a serious failure of the coating unless or until the coating as a whole over the area of rain impingement has become rotted or degenerate. An interlacing network of cracks appears to serve this purpose and to lead to drastic failure.

At a velocity of 600 mi/hr the mode of failure is the production of a chevron pattern along the trajectories of water flow from the impinging drops. There is a notable cementitious deposit especially on the ends of a specimen that was tested at a velocity of 600 mi/hr whereas this deposit is negligible when the test is carried out at a velocity of 500 mi/hr . Precipitation of calcium salts appears to occur in the water of the intercepted drops when solid specimens are rotated through the artificial rain of tap water at a velocity of 600 mi/hr. The hardness in parts per million of calcium carbonate for the tap water used is 22. This is a relatively low hardness.

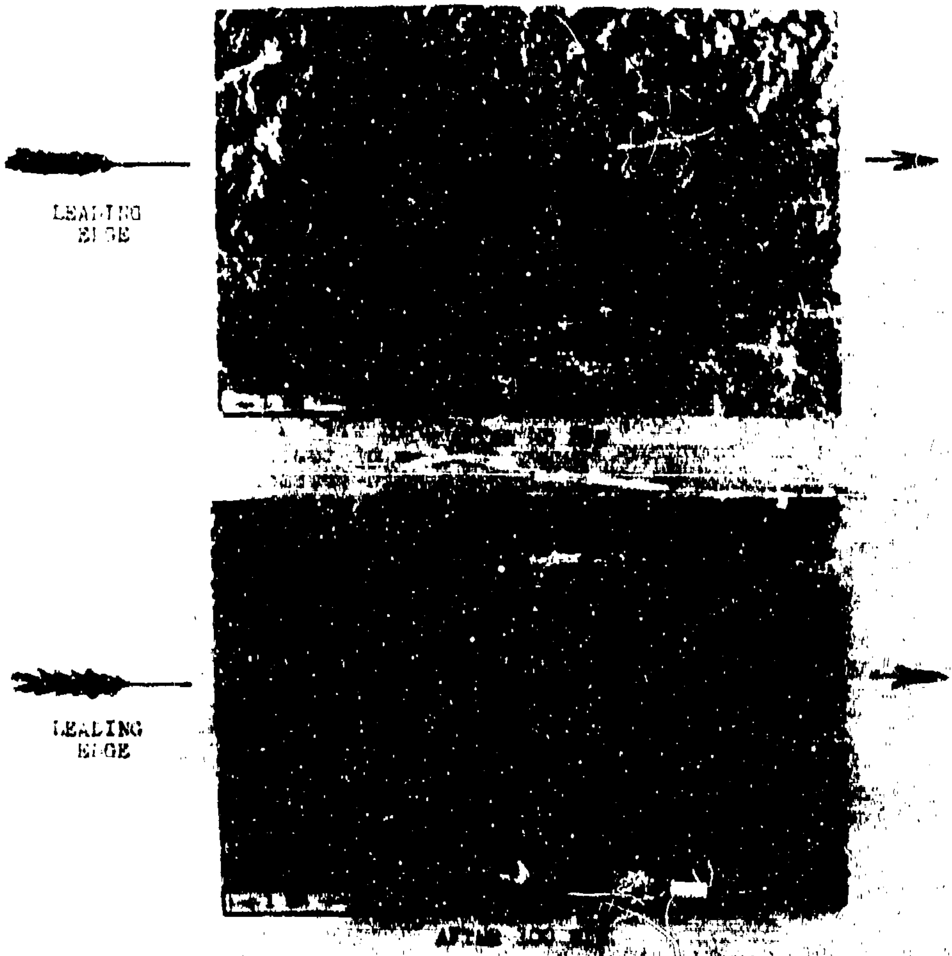


FIGURE 18 VIEWS OF GOODYEAR 23-56-BOSTIK 1007 NEOPRENE COATINGS AFTER TWO INTERVALS OF TEST AT A VELOCITY OF 500 MI/HR IN 1-IN/HR RAIN

The boiler-scale equation is

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

and the equilibrium reaction is forced to the right by loss of the gaseous product. It is possible that the loss of carbon dioxide may be caused in the open system of a colliding waterdrop by the impact pressure or by a temperature rise in the water of the drop as a result of the high-speed collision.

In an effort to throw some light on the mechanism that produced precipitation, experiments of a preliminary nature were performed in which concentrated solutions of calcium bicarbonate were irradiated with sound. It was found that precipitation of calcium carbonate only occurred if the solution was allowed to become warm during the irradiation.

The fact that mineral salts precipitate in the water of the artificial rain drops as they collide with a rapidly moving solid is important in the problem of testing the resistance of materials to high-speed rain-erosion damage. It is especially important in studies of the mechanism by which this type of damage occurs because the erosion damage is partly caused by the flow of the impinging waterdrops. The erosive action of the flow of water that is carrying a precipitate is more destructive than that of the flow of water alone; it is a serious problem in dredging pumps and hydraulic turbines. Erosion due to flowing water that is carrying a precipitate results from the collision of particles suspended in the water against the solid surface over which the flow occurs and by the dragging of these particles over the solid surface under the action of hydrodynamic forces.

Ilgaz [7] has studied the wearing of a plane surface by a sand-laden jet of water. He found that the equation

$$U = k\ S^{0.7}\ C_T^{\ 0.7}\ V_o^{\ 2.7}$$

where U is the rate of wear, k is a proportionality constant, C_T is the concentration of the transported material, V_o is the

velocity of the mixture, and S is the cross section of the jet, could be used to describe the results. A picture of the wear produced on rubber by impingement of such a jet is similar to the wear pattern produced on a neoprene coating during test on the rotating arm apparatus in an artificial tap water rain at a velocity of 600 mi/hr. In the case of the impinging sand-laden jet the wear grooves are radial lines from the stagnation point, that is, the wear grooves are in the direction of the water flow. In the case of the airfoil-shaped rain-erosion specimens coated with neoprene, the wear grooves are chevron-shaped, that is, the wear grooves are also in the direction of the water flow down and away from the leading edge of the airfoil shape.

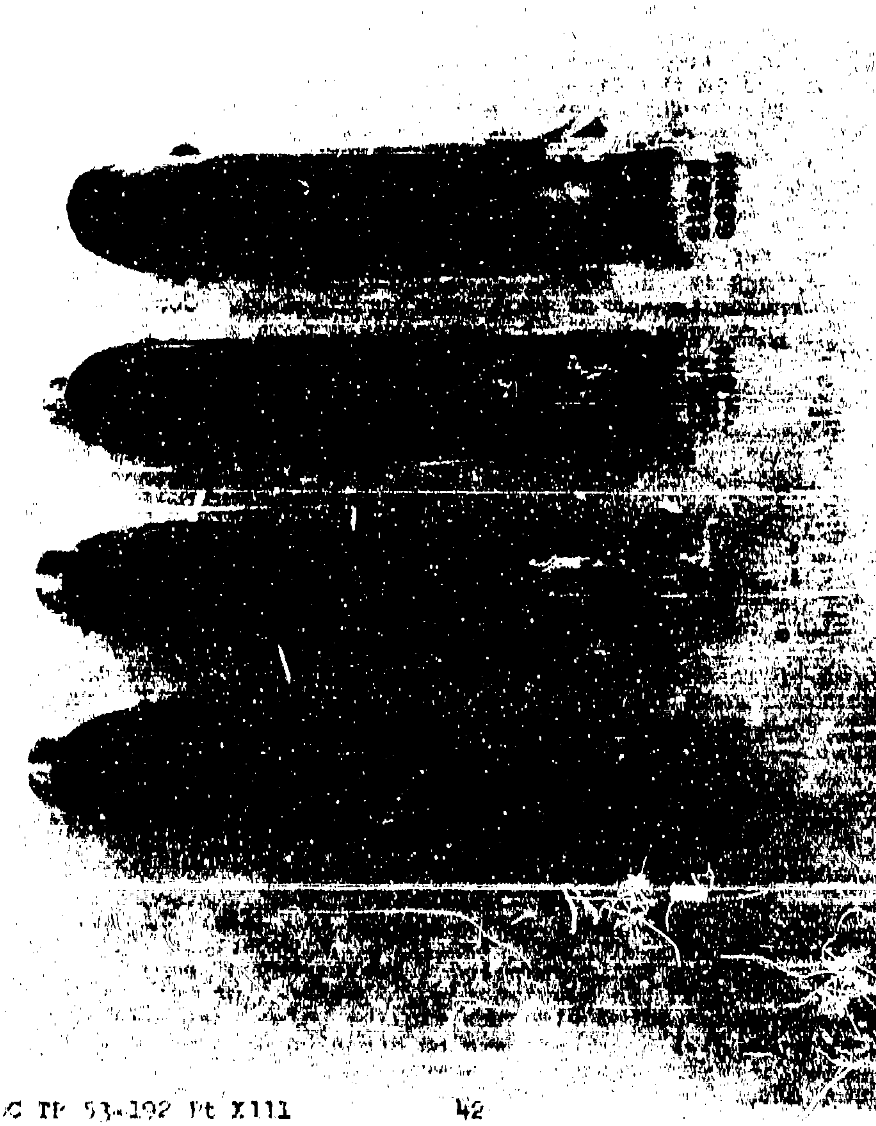
The effect of the flow of grit-laden water may be more serious on one material than on another; it is, furthermore, not a genuine aspect of real rain impingement. Consequently, it may cause divergence of test results from what is found under service conditions. Every effort should be made to remove this undesirable feature from the rotating-arm rain-erosion test.

A further discussion of the effect of hardness in the water used for the artificial rain is given in Section 4.1.1.

3.3.2.3 Gaco N-79 Neoprene over Gaco N-15 Primer

The specimens coated with Gaco N-79 neoprene over Gaco N-15 primer were numbered 2121 A and B and 2122 A and B. A picture of the eroded specimens is shown in Figure 19. Specimen 2121 A was tested for 10 min at a velocity of 600 mi/hr in 1-in/hr rain. Microscopic inspection of this specimen showed that there was a scattering of small round holes down the leading edge. There were also quite a few much smaller holes that may possibly have been produced by the tearing loose of grains of coating because this coating was very grainy in structure. There was no evidence of a chevron pattern in this Gaco coating. At high magnification some evidence of what might be the initiation of sutures could be seen.

Specimen 2121 B was tested for 20 min under the same conditions of velocity and rain rate. Microscopic inspection of this specimen again revealed a scattering of small round holes down the leading edge. The coating was, furthermore, peppered with the smaller holes that were noted on specimen 2121 A. There was an abrasion or tearing away of surface layers especially around the small holes of both sizes. There was no evidence of a chevron pattern



[illegible] 19 [illegible] SPECIMENS THAT WERE COATED WITH GACO N-[illegible] NEOPRENE

in the neoprene. At high magnification there was evidence of the initiation of sutures or cracks in the coating.

Specimen 2122 A was tested for 40 min under the same conditions of velocity and rain rate. There was a general abrasion of the surface of this specimen and many of the very small holes that were noticed on specimens 2121 A and B. There were quite a few sutures or cracks in the coating. There was a tearing out of pieces of coating from the surface at the high-spedd end. There was also a peeling or tearing back of the coating from the extreme edge of the high-speed end. A valid comparison between the Goodyear 23-56 and Gaco N-79 coatings cannot be made on this point, however, because the Goodyear 23-56 coating had been applied not only on the specimen but also on the shoulders where the clips fasten the specimen to the propeller so that the edge of the coating was protected from the colliding waterdrops; in the case of the specimen coated with Gaco N-79 the shoulders had been left bare of coating so that the water from the impinging drops had access to the edge of the coating. There was an indistinct chevron-like pattern in the neoprene of this specimen; it exists at the high-speed end of the specimen whereas the chevron pattern in the Goodyear 23-56 neoprene appeared in the low-speed end of the specimen.

Specimen 2122 B was tested for 60 min under the same conditions of velocity and rain rate. Microscopic inspection of this specimen revealed increased abrasion wear and tearing out of pieces of coating material from the surface. The coating was also peeled or torn back extensively from the extreme edge of the high-speed end where the impinging drops had access to the edge of the coating. There was an indistinct chevron-like pattern in the neoprene of this specimen mainly at the high-speed end. There were many sutures or cracks in the coating.

In general it can be said that the white neoprene failed prematurely due to loss of adhesion; the intrinsic resistance of the coating itself was essentially not tested. Although the adhesion failure of the Goodyear 23-56 was less drastic than that of the white neoprene, it showed definite adhesion failure. At the end of 40 min of test the

Gaco-N-79-Gaco-N-15 system showed more abrasion than the Goodyear-23-56-Bostik-1007 system but the Goodyear coating had lost adhesion so that it failed drastically at the end of the 60-min test period whereas the Gaco coating had not as yet failed drastically. Adhesion appeared to be the weakness-leading-to-failure of the Goodyear coating; graininess appeared to be the weakness-leading-to-failure of the Gates coating. Both coatings developed sutures or cracks.

The small round holes that were observed in both the Good~~year 23~~-56 and the Gaco N-79 coatings are very likely due to air bubbles. The bubbles may have risen to the surface and burst during the cure of the coatings or the bubbles may have risen close to the surface during the cure and may have burst only when they were struck by intercepted waterdrops.

The very small holes that were only characteristic of the Gaco N-79 coating may be the result of the tearing out of grains of this very grainy coating. The number of these holes appeared to increase with the length of the test time. The holes of both sizes appeared to provide a foothold for abrasion failure of the Gaco-N-79-Gaco-N-15 system. Material was torn out from around the holes.

In general the failure of the three neoprene coatings in rain erosion test was in agreement with the predictions made for them on the basis of their resistance to impingement with oil-filled gelatin capsules and with deforming lead pellets.

4. Possible Modes of Failure of the Neoprene Topcoat

The most probable mechanisms that may be responsible for the failure of the neoprene topcoat are the rubber abrasion that has been referred to extensively throughout this report, chemical deterioration and mechanical fatigue. These mechanisms are discussed in the following sections.

4.1 Rubber Abrasion

The process of abrasion is not clearly understood. There appear to be as many abrasion mechanisms as there are ways of producing abrasion on surfaces. Experimental work that has been done on the moving of one metal surface over another without lubrication indicates that this process is not continuous but is characterized by a "stick-slip" behavior. Bowden and Leben [8] state that their experiments suggest that friction is due to a welding together of the metals at local points of contact. This is the "stick"-step. They regarded these junctions as being large compared with the dimensions of a molecule and concluded that when they are broken the metal is distorted to a considerable depth. The breaking of the junctions is the "slip"-step and is accompanied by a temperature flash. Morgan, Muskat, and Reed [9] later concluded that melting is not necessary to establish the "stick-slip" behavior and ascribed the temperature flashes on the "slip"-step to dissipation of energy.

The abrasion of rubber is also a "stick-slip" process. Schallamach [4,5,6] has found that the abrasion trace left by a needle on a pure gum vulcanizate rubber is not continuous. It consists of isolated pits or tears; the surface material between the pits or tears is undamaged. In regard to the abrasion caused by a needle, Schallamach postulated that (a) the needle pricks a small hole in the rubber, and, as the needle moves, a bulge of rubber is built up in front of it; eventually, (b) the needle moves over this bulge simultaneously pulling out a thong of rubber that breaks either at its root or at the needle tip. Step (a) is the "stick"-step and step (b) is the "slip"-step. See Figure 20. The mechanism of needle abrasion postulated by Schallamach depends on two factors, namely, the bulge of rubber must adhere by friction to the tip of the needle against the pull of the elastic forces, and the tensile properties of the material must admit of large deformation without failure.

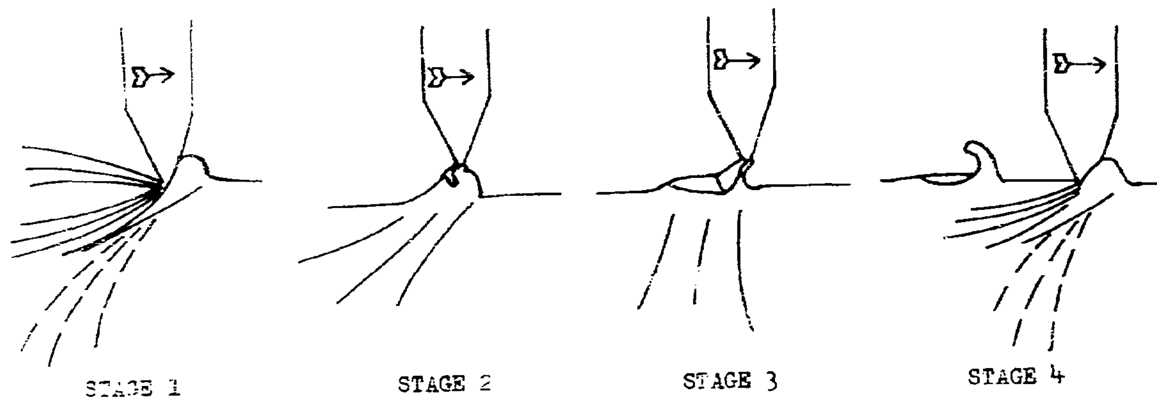


FIGURE 20 A SCHEMATIC REPRESENTATION OF THE "STICK-SLIP" PROCESS OF RUBBER ABRASION

Schallamach has found that an array of nearly parallel ridges is often produced on rubber surfaces by abrasion. He refers to this array as the "abrasion pattern". The ridges of the abrasion pattern run at right angles to the direction of abrasion and are asymmetric with respect to this direction. They are characterized by overhanging crests that lean against the direction of abrasion. According to Schallamach the ridges are all bent backwards during the abrasion and material is "removed by abrasion" from what in the relaxed state was the underside of the ridges. Schallamach remarks that the origin of the abrasion pattern is not yet fully understood and states that it "is most probably a consequence of the combination of high elasticity and high coefficient of friction which is characteristic of rubber".

In view of the observation that the circles of damage produced on a 10-mil thickness of MMM EC-539 neoprene by the impingement of waterdrops may be the result of an abrasion process, some elementary observations of the abrasion of this rubbery coating were made. An abrasion similar to that observed by Schallamach was found to result when a sharp-pointed tungsten carbide marking needle was drawn across the surface of the coating. See pictures 1 and 2 of Figure 8. The damage is discontinuous and consists of a succession of pits or tears. The flap of rubber torn out of the surface in the making of each of these tears recovers in such a way that it points in the direction from which the marking pencil was moving. In pictures 1 and 2 of Figure 8 the marking pencil was moving downward and it can be seen that the flaps of rubber ripped up in making the individual tears point upwards.

The abrasion of this rubbery coating that results when a razor edge is drawn across it was also observed. Irregularities along the razor edge produce a result that is equivalent to that which would be produced by a series of needle points moving along a line. See picture 3 of Figure 8. From time to time the cut in the rubber is continuous over the space of several of the irregular protrusions on the razor edge. The flaps of rubber that are raised from the surface again point in the direction from which the razor edge moved, that is, toward the left of the picture.

The needle is able to grip the rubber and to force the rubber up into a bulge as it moves only because the coefficient of friction between the needle and the rubber is high. If, indeed, high-speed rain erosion progresses by a similar mechanism on neoprene the extent of erosion damage on comparable specimens should be reduced on a specimen for which the coefficient of friction between the radially flowing water from the drop and the rubber surface is reduced. Roth, Driscoll, and Holt [10] have found that graphite and caster oil reduce the coefficient of friction between rubber and steel. They found that these materials also serve to prevent increase of the coefficient of friction between rubber and steel with increase of speed of the relative motion of the rubber and steel surface. In an effort to obtain evidence with regard to the hypothesis that neoprene erodes by abrasion under waterdrop impingement the effect of applying graphite, oil, and detergents to neoprene coatings during rain erosion test was explored.

4.1.1 Effect of Hardness in the Water Used for the Artificial Rain and of the Use of a Wetting Agent in the Water

Eight airfoil specimens were fabricated and coated with neoprene at the Cornell Aeronautical Laboratory. The specimen-bases were of 2024 aluminum alloy. They were lightly sanded and cleaned with a cloth dampened in toluene. One coat of Bostik 1007 primer and 14 coats of Goodyear 23-56 neoprene were brushed on the specimens; 15 min air dry was allowed between coats. The dry film thickness was approximately 16 mils. The coatings were cured at room temperature for 10 days. They were numbered 1893 A and B through 1896 A and B.

Specimens 1893 A and B were tested at a velocity of 500 mi/hr in 1-in./hr artificial rain. Ordinary hydrant water having a hardness of 22 ppm was used to make the artificial rain. The Cornell Aeronautical Laboratory reported that the coating started to erode in 12 min. The test was stopped at the end of 50 min. At the end of this length of time the high speed end of the leading edge of each specimen was strongly eroded; the low-speed end was eroded to a lesser degree. See picture 1 of Figure 21. Inspection of these specimens showed very little, but some, evidence of a cementitious deposit from the water.

SPECIMEN 1893 A HIGH SPEED END

TEST VELOCITY 500 MI/HR

SPECIMEN 1896 B SHOWING UNDERSIDE OF TURNED BACK FLAP OF COATING

TEST VELOCITY 600 MI/HR

FIGURE 21 VIEWS OF GOODYEAR 23-56-BOSTIK 1007 NEOPRENE AFTER EROSION TEST

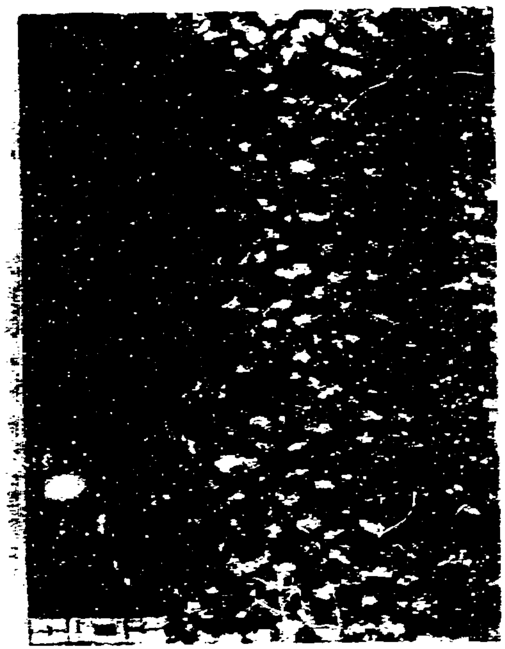
Microscopic inspection showed the presence of isolated, surprising round, small holes especially on the low speed end of specimen 1893 B. Deep circular holes that were surrounded by a torn-out area were observed. This may be evidence that the coating was torn away around holes of this kind by the radial flow of drops after the holes themselves had formed. In the case of at least one such round hole on specimen 1893 B, a thin layer of coating material that was about the size of the mouth of the hole appeared to be lying on the bottom surface of the hole. This observation may indicate that these holes are formed when the thin skin of coating over bubbles, which exist in the coating itself and which are near the surface, is broken in.

The process of erosion appeared to be the tearing away of thin segments of coating material at the surface of the coating. After a roughened surface is formed, further erosion could be expected to progress rapidly because the impact pressure of additional drops that impinge is multiplied in depressions of the surface roughness and the velocity of the radial flow, which governs its ability to tear more of the coating away, is increased. Cuts or tears which could be due to attack of the neoprene by ozone or by hydroxyl ion were also evident in the roughened surface of the coating on specimen 1893 B. Qualitatively similar damage features were observed on specimen 1893 A. Uneroded areas on the sides and away from the leading edge of both specimen 1893 A and 1893 B were grainy in appearance.

Specimens 1894 A and B were eroded at a velocity of 600 mi/hr in 1-in./hr artificial rain for 140 min. The artificial rain was again of ordinary hydrant water having a reported hardness of 22 ppm. The only difference in the test conditions of specimens 1894 A and B and specimens 1893 A and B was the velocity at which the specimen struck the waterdrops of the artificial rain and the test time. Visual inspection of these specimens showed that although they were tested at a higher velocity and for a longer period of time than specimens 1893 A and B, they were eroded to a lesser degree. Microscopic examination indicated that the erosion was also of a different character.

The low-speed end of the leading edge was characterized by a chevron pattern of erosion in the neoprene coating. See picture 1 of Figure 22. The point of the chevron faced the

SPECIMEN [illegible] A, LOW SPEED END



2

SPECIMEN 1894 A, HIGH SPEED END

FIGURE [illegible] SURFACE OF GOODYEAR 23-56-BOSTIK 1007 NEOPRENE AFTER EROSION TEST AT A [illegible]
OF 600 MI/HR

low-speed end of the specimen. The eroded surface was rippled but was surprisingly smooth and almost free of the erosion characteristics that were found on specimens 1893 A and B although a few round holes and torn-out areas could be seen. At the high-speed end of the leading edge of the specimen the chevron pattern was almost obliterated by a generally beady texture of the eroded surface. See picture 2 of Figure 22. Cracks that could be due to attack of the neoprene by ozone or by hydroxyl ion could be seen. A cementitious mineral deposit existed at both ends of the specimen. The appearance of specimen 1894 B was qualitatively similar.

Specimens 1895 A and B were tested under the same conditions and for the same length of time as were specimens 1894 A and B but the water used for the artificial rain was passed through a softener and was reported by the Cornell Aeronautical Laboratory to have a hardness of less than 2 ppm. These specimens eroded in a manner similar to that of specimens 1894 A and B. Cementitious deposits were observed at both ends of these specimens showing that the softened water used for the artificial rain contained enough hardness to allow precipitation to occur. The chevron pattern at the low-speed end of the leading edge was less distinct than on specimens 1894A and B but the beady texture of the surface at the high speed end was about the same. The Cornell Aeronautical Laboratory reported that in the case of specimens 1894 A and B the chevron pattern was first detected after 25 min of test but that in the case of specimens 1895A and B it appeared only after 40 min of test. This observation appears to indicate that the chevron pattern is related to the amount of hardness in the water and hence to the amount of cementitious precipitate that can come out of it. The observation that the general beady texture at the high-speed end of the specimen after the same test time (140 min) was about as distinct as on specimens 1894A and B seems to indicate that it may be a result of the water flow and/or of the texture of the neoprene coating more than of the amount of precipitate present in the water. There were quite a few sutures or cracks in the coating on both specimens.

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Specimens 1896 A and B were tested under the same conditions as specimens 1895 A and B except that the total test time was 130 min and that 1.0 g of Hyamine 1622 germicidal wetting agent was added to each 0.5 gal of water that was used to make the artificial rain. The addition of the wetting agent reduced the surface tension of the softened water from 75 d/cm to 35 d/cm. The Cornell Aeronautical Laboratory reported that the Goodyear 23-56 neoprene coating appeared to be softer on these two specimens and that a chevron pattern similar to that which appeared on specimens 1895A and B was detected after 40 min of test.

Microscopic inspection of these specimens showed the presence of a cementitious deposit at both ends. The erosion was similar in appearance to that which formed on specimens 1895 A and B, namely, a dim chevron pattern at the low-speed end and a beady structure of the surface at the high-speed end. There were a few round holes and torn-out spots. On specimen 1896 B a section of coating was turned back so that the reverse side of it (the side that had been bearing against the aluminum alloy specimen-base) could be seen. The reverse side of the coating had a beady structure without having suffered erosion at all. See picture 2 of Figure 21. This observation appears to indicate that the beady structure of the surface that formed at the high-speed end of the specimens during test is related to the coating itself as well as to the water flow or to the presence of a precipitate in the water. The presence of globules or beads in the coating could result from use of neoprene that was not efficiently dispersed during compounding or it could be due to the use of old material in which partial coagulation has occurred. Addition of diluent to such material would not disperse the aggregates. Inspection of a torn edge of the coating on specimen 1896 B showed some evidence of separation of layers of the coating. Both specimen 1896 A and specimen 1896 B contained many sutures or cracks that could be due to attack by ozone or by hydroxyl ion.

4.1.2 Effect of Detergent Applied to the Coating

Four airfoil specimens were fabricated of 2024 aluminum at the Cornell Aeronautical Laboratory. They were coated with Bostik 1007 primer and with Goodyear 23-56 neoprene (brush coat). After air drying for one week, the specimens were

dried in a dessicator overnight and were then weighed on a chemical balance. Two of the specimens (Cornell Aeronautical Laboratory numbers 1400 A and 1401 A) were brushed with a concentrated solution of alkyl aryl sulfonate and were air dried for at least one hour. Each of these specimens was tested with an untreated control specimen (Cornell Aeronautical Laboratory numbers 1400 B and 1401 B) at a velocity of 600 mi/hr in 1-in./hr artificial rain. After each 10-min interval of the first two hours of the test, the four specimens were dried in a dessicator overnight and were then weighed before another film of detergent solution was applied to the treated specimens. This procedure was repeated at 20-min intervals during the remainder of the test. The weight losses of these specimens at the end of the 10-min intervals of test during the first two hours of test are plotted in Figure 23.

Inspection of the eroded specimens at X 20 magnification revealed that specimens 1400 A (treated with detergent) and 1400 B (control), which were tested for a total of 260 min, were in about the same state of erosion. There was a fairly distinct chevron pattern at the low-speed end of these specimens and small coating bubbles and torn-out spots at the high-speed end. Specimen 1401 A (treated with detergent) appeared to be slightly more eroded than specimen 1401 B (control). These specimens were tested for a total of 320 min. There was a strong chevron pattern at the low-speed end, a general beadiness in the central part of the leading edge, coating bubbles over most of the leading edge, and torn-out spots at the high-speed end of these specimens. All four specimens contained quite a few cracks or sutures that may be due to attack of the neoprene by ozone or by hydroxyl ion.

The microscopic inspection showed that there was little if any difference in the appearance of the specimens treated with the alkyl aryl sulfonate and the controls. From this it can be concluded either that the alkyl aryl sulfonate washed off too soon to be of any real benefit or that it was of little consequence to the erosion damage whether the surface of the coating was hydrophilic or hydrophobic.

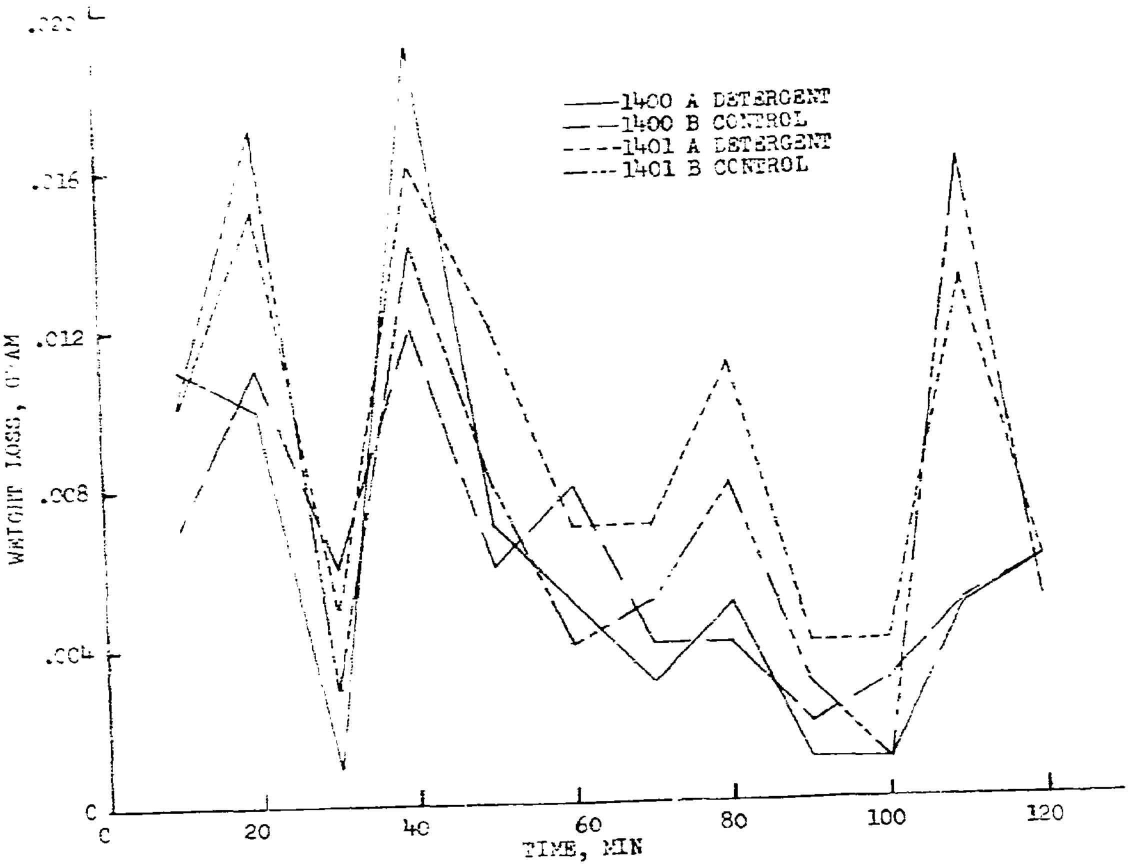


FIGURE 23 WEIGHT-LOSS-VERSUS-TIME CURVE FOR FOUR NEOPRENE COATED SPECIMENS TWO OF WHICH WERE TREATED WITH DETERGENT DURING TEST

From Figure 23 it can be seen that the weight loss sustained by the specimens in equal intervals of time is not constant. During the first two hours of test, peak losses occurred in the intervals 10 to 20 min, 30 to 40 min, 70 to 80 min, and 100 to 110 min. This seems to indicate that there are preparation periods, in which little or no erosion loss occurs, followed by periods in which loss is accomplished. The preparation periods may be characterized by the development of structures without loss of material, such as coating bubbles, which are later torn open with loss of material. The development of surface cuts, cracks, or tears without loss of material may, similarly, be followed by a tearing away of small pieces of the coating when the water from additional impinging drops is driven into them, or by the falling away of pieces of coating material from between circumscribing cracks.

While the erosion leading to the chevron pattern in the neoprene at the low-speed end of the specimen appears to be a gradual wearing through of the coating itself by the flow of grit-laden water, it appears that erosion due to the high-speed intercepting of waterdrops may be the result of the gradual development of coating bubbles due to loss of adhesion between the coating and the specimen-base followed by loss of the coating material that formed the bubble, the gradual etching out of coating granules or of foreign particles in the coating followed by loss of the granules or particles, and the gradual development of surface cuts, cracks, or tears followed by the removal of material around them, or between them.

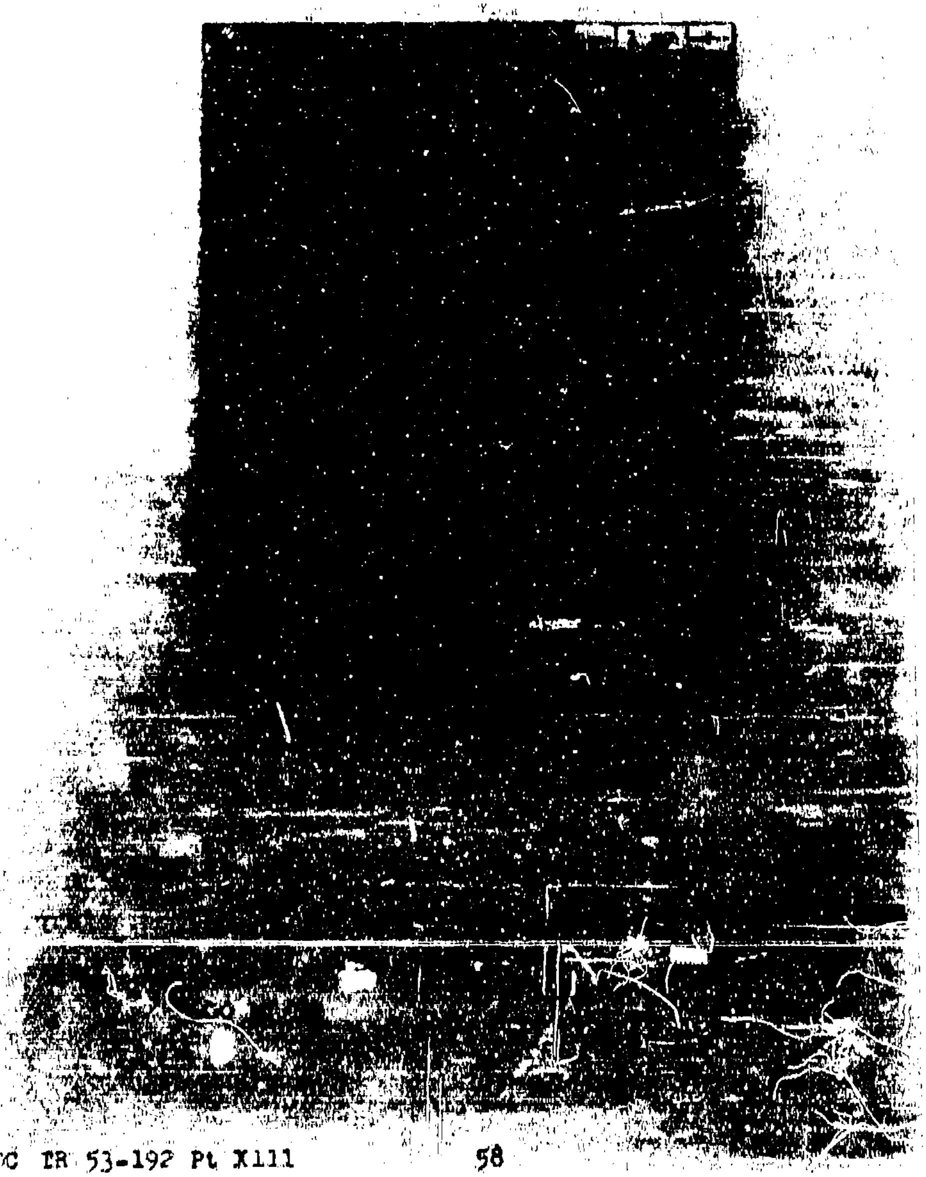
4.1.3 Effect of Graphite and Oil Applied to the Surface of the Specimen

Four airfoil specimens were fabricated, coated with neoprene, and tested for rain erosion resistance at the Cornell Aeronautical Laboratory. The specimen-bases were of 2024-O aluminum. They were coated with Bostik 1007 primer and with 10 mils of Goodyear 23-56 neoprene. After a 10-day air dry, the specimens, which were numbered 1390 A and B and 1391 A and B, were tested for rain-erosion resistance at a velocity of 600 mi/hr in 1-in./hr artificial rain. One specimen was rubbed with colloidal graphite (Aquadag) and another was rubbed with castor oil at 10-min intervals during the test; two of the specimens were tested as controls, that is, without a surface treatment.

It was reported that when the whirling arm was stopped after each 10-min interval of test, the films of graphite and caster oil appeared to have been washed off the leading edge, and that visual examination of the coatings on these specimens at the end of 75 min of test showed no appreciable difference in the amount or type of erosion. The time to erode through the coating was in each case 70 min with the exception of specimen 1390 B for which it was 68 min.

Inspection of these specimens with a stereoscopic microscope produced the following observations. There were many small round holes in the coating on specimen 1390 A, which had been rubbed with graphite at 10-min intervals during the test. These round holes were surrounded with a collar of the coating material and appeared to have been air bubbles in the neoprene that were near the surface and that had been broken open by the waterdrop blows. There was a dim chevron pattern in the coating at the low-speed end of the specimen and a beadiness at the high-speed end which was of a finer texture than that observed on specimen 1894 A. There were also large coating-bubbles that had been squashed by the waterdrop blows. These bubbles involve the entire thickness of the coating and form as a result of loss of adhesion between the coating and the specimen-base to which it was applied. There were also short cracks or sutures in the coating.

The coating on specimen 1390 P, which was a control that had no surface treatment, is peppered over the entire leading edge with many round small holes (See Figure 24) that have a raised collar of neoprene around them. They may have been caused by air bubbles in the coating that were broken open by the waterdrop impacts. Some small bumps exist that have no hole in them and it is possible that these are air bubbles in the neoprene that are near the surface. There is a dim chevron pattern in the coating at the low-speed end of the specimen and a pebbled structure at the high-speed end of it that is fine in texture in comparison with the beady structure of specimen 1894 A. Coating-bubbles that involve the entire thickness of the coating also exist; two of these have been torn open so that the surface of the 2024-0 specimen-base can be seen. Many cracks and sutures also can be seen in the coating.



There was a dim chevron pattern in the neoprene at the low-speed end of specimen 1391 A, which was rubbed with castor oil. The chevron pattern on this specimen was less distinct than that on the other specimens used in this study. A pebbled structure of the surface, which was of a finer texture than that on specimen 1894 A, existed at the low speed end of the specimen and extended to the high-speed end. There were spots where the coating appeared to have lost adhesion; at the high-speed end it was torn open to the 2024-O aluminum specimen-base. There were also short cracks or sutures in the coating. Observations made on specimen 1391 B were similar to those on specimen 1391 A.

There is very little difference in the degree of erosion that was produced on specimens 1390 A and B and on specimens 1391 A and B. This appears to indicate that the use of graphite or oil has little, if any, effect in retarding or in mitigating the erosion. The chevron pattern in the neoprene at the low-speed end of specimen 1391 A was less pronounced than that on the low-speed end of the other specimens used in this study and this may indicate that oil on the surface of the specimen does afford some protection against the flow of the waterdrops after they impinge.

An additional test of the effect of application of oil to the specimens was made using silicone oil, which it was thought might be more tenacious than the castor oil that was used. Four 2024-O aluminum alloy airfoil shaped test specimens were fabricated at the Cornell Aeronautical Laboratory and were brush coated with Goodyear 23-56 neoprene using Bostik 1007 as the primer. The coating thickness was approximately 11 mils. After air drying for five days the specimens were placed in a desiccator overnight; they were then weighed. Specimens 2378 A and 2378 B were brushed with a thin film of silicone oil (viscosity 300 centistokes) prior to rain-erosion test at a velocity of 500 mi/hr in 1-in./hr rain. Specimens 2379 A and 2379 B were not coated with the silicone oil. At the end of a 5-min test interval the specimens were stored in a desiccator overnight and were weighed again. Specimens 2378 A and B were then brushed again with silicone oil and the cycle of procedure was repeated. The total test time accumulated on the specimens was from 60 to 70 min. The weight losses that were sustained by the specimens are shown graphically in Figure 25.

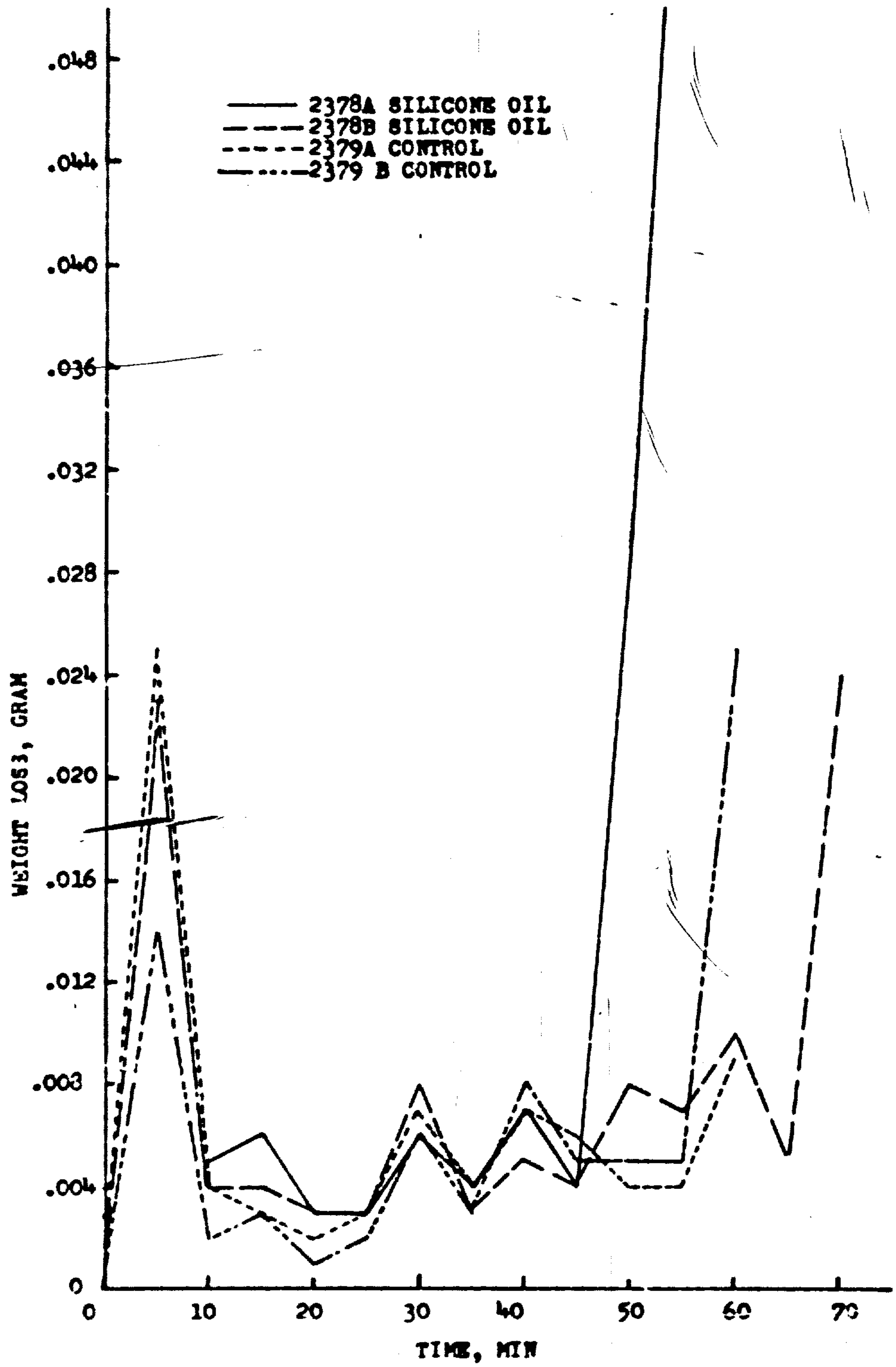


FIGURE 25 WEIGHT-LOSS VERSUS TIME CURVE FOR FOUR NEOPRENE COATED SPECIMENS TWO OF WHICH WERE COATED WITH SILICONE OIL DURING TEST

Microscopic examination of the specimens led to the conclusion that the type and degree of damage that was sustained by the oil-treated specimens and by the control specimens was about the same. In general, it consisted of a dim chevron pattern at the low-speed end of the specimen and of broken out spots at the low-speed end which increased in density toward the high-speed end until at the high-speed end there was a swath down the center of the specimen from which a complete layer of coating material had been removed. There was evidence of crack formation in the coating at both ends of the specimens.

4.2 Chemical Deterioration

Ozone is the main factor in the deterioration of elastomers during weathering [11]. It is responsible for the regular cracking that forms perpendicular to the axis of any localized stress in the rubber; it is also responsible for the irregular cracking or crazing which was formerly attributed to light-activated oxidation [12]. The essentials required for the ozone deterioration of a susceptible elastomer (all elastomers that contain double bonds are susceptible) are ozone and tension stress [11, 13]. Rubber and butadiene elastomers have a critical stress or strain above and below which ozone cracking is less severe; neoprene vulcanizates become more susceptible to ozone attack as stress and strain are increased [13]. Neoprene vulcanizates must be subjected to both stress and strain of an appreciable degree before they will crack under the influence of ozone [13]. The stretch required for vulcanized natural rubber is 5 to 25 per cent; the stretch required for vulcanized neoprene is about 50 per cent [15]. However, when it is freely exposed to air and light chloroprene darkens and becomes harder especially on the surface [14]. These changes are accompanied by the liberation of hydrogen chloride [14]. It has been pointed out that the presence of a chlorine atom at a double bond decreases the tendency of the double bond to react with ozone and that in chloroprene the chlorine atom is attached to a carbon atom having a double bond [14].

The characteristic cracking of stressed rubber that results when it is exposed to ozone can also be produced by exposing it to free radicals [16]. Cracking by tertiary

butoxy, phenyl, benzoyl, acetyl, and hydroxyl radicals has been observed [16]. It is possible that the failure of neoprene coatings under high-speed rain impingement is in some measure a consequence of attack either by ozone or by the hydroxyl ions that are produced when waterdrops are intercepted by a solid surface at high speed.[b] When a 2-mm waterdrop is intercepted at a velocity of 600 mi/hr the kinetic energy of the collision is 3.6×10^{-5} kcals. The heat required to ionize a mole of water with the resulting ions at infinite dilution (no ionic interactions) is 13.4 kcals. A 2-mm drop of water is about 2.3×10^{-4} moles. Therefore, the heat required for ionization of a 2-mm drop of water is 3.1×10^{-3} kcals with the ions at infinite dilution. Because the kinetic energy of the collision of the drop with the solid surface is 1/100 of the energy required to ionize all of the water contained in the drop, ionization can be expected to occur.

When a waterdrop is intercepted at high speed by a rubber-coated solid surface, it first exerts a compressive load on the rubber coating. The waterdrop then flows out radially and the radial flow of water from the drop imposes a radial stretch on the rubber coating around the point of impingement. It is possible that ozone addition or hydroxyl ion addition to the double bonds of the rubber may occur during a stretch-and-recover cycle and that cracking or a fine surface crazing may result from the stresses, stretches, and chemical additions that may occur during successive waterdrop blows.

Natural rubber is more susceptible to ozone attack than neoprene. Natural rubber in the form of vulcanized sheet stock has been tested for rain-erosion resistance; it was found to be less rain-erosion resistant than neoprene. It was decided to incorporate the antiozonant N, N' di-tridecyl-p-phenylenediamine into natural rubber and to prepare sheets of this material that could be bonded to rain-erosion test specimens. Eight sheets of rubber were prepared that contained the antiozonant; four of these contained heliozone wax and four contained no wax. Four sheets of rubber were prepared that contained neither antiozonant nor wax. These rubber sheets were sent to the Cornell Aeronautical Laboratory

[b] The possibility that ozone cracking may be involved in the rain erosion failure of neoprene coatings was suggested by Dr. L. A. Wood and Mr. Frank Roth of NBS Rubber Section. The thought that water fragments may be involved was suggested by Mr. Max Tryon of NBS Rubber Section.

to be bonded to rain-erosion test specimens with adhesive and tested. These rubber sheets were not tested; the Cornell Aeronautical Laboratory reported that they had no success in bonding the rubber sheet to rain-erosion specimens ~~with adhesive~~.

It was then decided to use an antiozonant on the standard neoprene coatings to determine whether or not the test life of the very ozone-resistant neoprene would be increased at all. A sample of N,N' di-octyl-p-phenylenediamine (U.O.P. No. 88) antiozonant, which is applied externally, had been sent to the Cornell Aeronautical Laboratory. It was requested that rain-erosion specimens be coated with the standard neoprene coatings and that they be tested for rain-erosion resistance with and without external application of this antiozonant. The results of the rain-erosion tests that were run are given in Table 3.

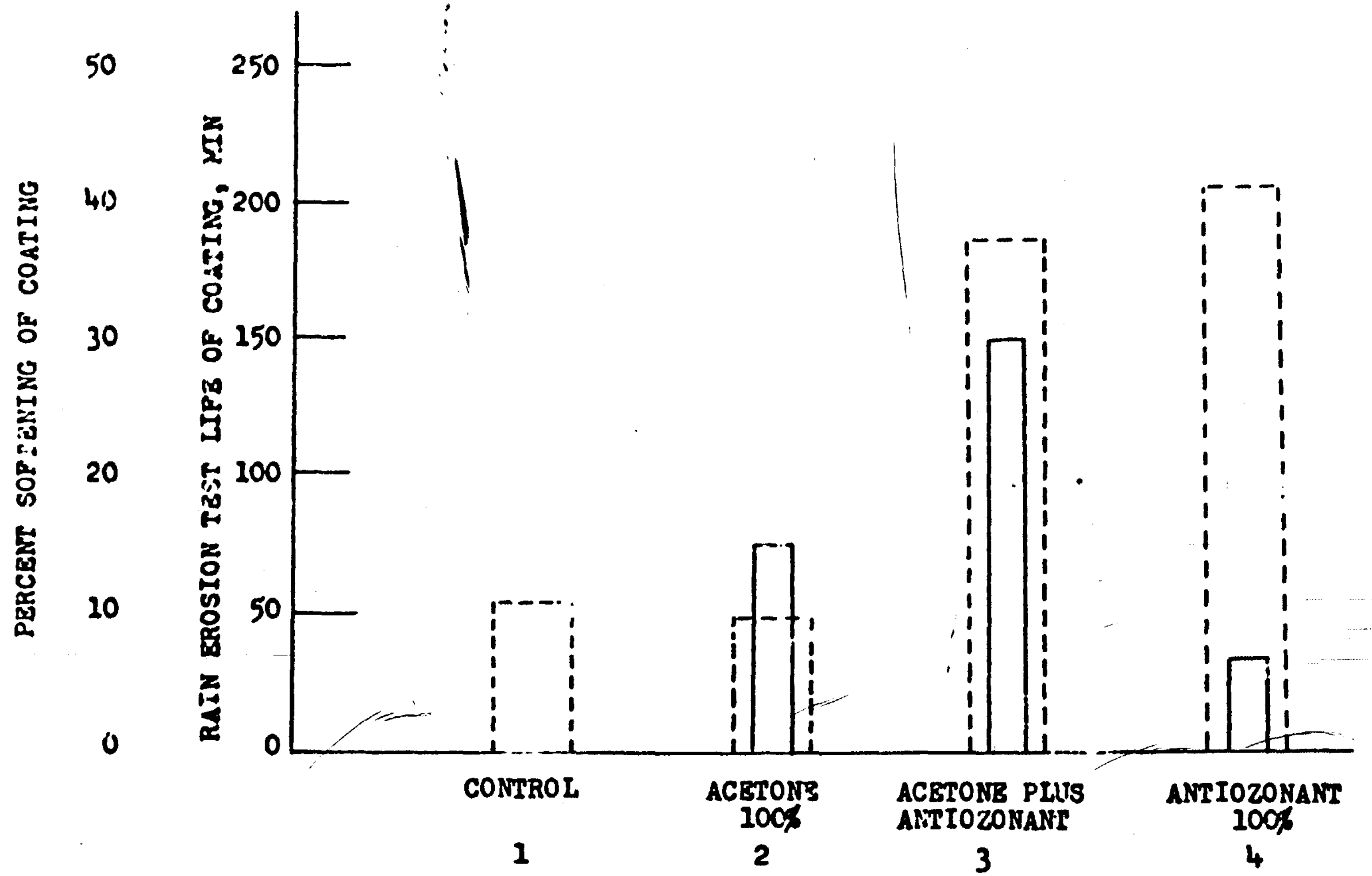
Only two specimens that were treated with antiozonant were sent ~~to the~~ National Bureau of Standards for study. These were specimens 2387 A and 2387 B which had been treated with a 50 per cent solution of the antiozonant in acetone. The neoprene coatings on these specimens were applied over 2024-0 aluminum alloy specimen-bases. The coatings were of Goodyear 23-56 neoprene over Bostik 1007 primer; they were 10 to 12 mils thick. At the end of 5-min intervals during rain-erosion test at a velocity of 500 mi/hr, the specimens were dried with a cloth and the antiozonant solution was brushed on them as a thin film. Specimen 2387 A was tested for 190 min and specimen 2387 B was tested for 180 min before a hole eroded through the coating. Untreated controls lasted only 50 min before a hole eroded through the coating.

Microscopic inspection of specimens 2387 A and B showed that there was a dim chevron pattern eroded in the neoprene at the low-speed end of the specimen; the surface of the high-speed end had a pebbled appearance. There were a few pits scattered down the length of the leading edge. A turned back flap of coating on specimen 2387 B made it possible to see that the underside of the coating was uniform and without nodules such as appear on the underside of the coating shown in picture 2 of Figure 21. The outstanding difference between these eroded antiozonant-treated neoprene coatings and other eroded neoprene coatings was the absence of cracks or sutures. There appeared to be no evidence of crack formation. The failure that eventually occurred appeared to be the result of a loss of adhesion.

The results presented in Table 3 indicate that use of a 50 per cent solution of the antiozonant in acetone produced more than a threefold increase in the test life of the Goodyear 23-56-Bostik 1007 neoprene system and that use of 100 percent antiozonant produced very nearly a fourfold increase in the test life of this neoprene system. The increase in the test life of the Gaco N-79-Bostik 1007 neoprene system was nearly but not quite as much. It would be of interest to know the response of the Gaco N-79-Gaco N-15 neoprene system. It can be seen in the description of the coating failure that is given in Table 3 that whereas the control coatings and the coatings that were treated with 100 per cent acetone were pitted, the failure of the coatings that were treated with antiozonant was through eventual loss of adhesion that resulted in coating bubbles that later tore open.

The Cornell Aeronautical Laboratory reported that the neoprene coatings were softened by the antiozonant alone, by acetone alone, and by the solution of antiozonant in acetone. For the three reagents that were used to treat the coatings, the greatest swelling and softening resulted from the use of antiozonant-acetone solution and the least swelling and softening resulted from the use of 100 per cent antiozonant. Their data are presented graphically in Figure 26.

Treatment of the neoprene with 100 percent acetone had no effect on its rain-erosion test life. The acetone evaporated very rapidly. Softness of the neoprene coating that resulted from the use of 100 per cent acetone vanished with the acetone. Therefore, whatever effect the softening of the neoprene had on its rain-erosion test life must be determined from the results obtained on treatment with the acetone-antiozonant solution and treatment with 100 per cent antiozonant. A comparison of bar graph 3 with bar graph 4 in Figure 26 indicates that a 30 per cent softening of the coating is associated with a 180-min test life when acetone plus antiozonant was used whereas a 7 per cent softening is associated with a 220-min test life when antiozonant only was used. From these data it cannot be concluded that test life was determined by the softness of the coating. Furthermore, Beal, Lapp, and Wahl [17] have concluded that "in the neoprene rubbers tested, those with the greatest resiliency, lowest permanent set, and high Durometer hardness, had the best resistance to rain erosion". Softness would therefore not appear to be the correct explanation. It has been suggested that the



LEGEND: SOLID LINE BAR GRAPH GIVES PERCENT SOFTENING OF THE NEOPRENE AFTER IMMERSION IN THE SOLUTION FOR 30 MIN FOLLOWED BY A DRYING PERIOD OF 15 MIN

DOTTED LINE BAR GRAPH GIVES RAIN EROSION TEST LIFE IN MIN

FIGURE 26 EFFECT OF SURFACE TREATMENT OF GOODYEAR 23-56 NEOPRENE WITH AN ANTIOZONANT

Table 3
Test Results on Neoprene Coatings Treated with Acetone and with Antiozonant

C.A.L. Spec. No.	Coating System on 2024-O Aluminum Alloy Airfoils	Treatment	Erosion Through Coating	Remarks
2495 A	Goodyear 23-56 neoprene over Bostik 1007 primer (10-12 mils)	none	57 min	Moderate Pitting on high-speed half; scattered holes through coating.
2495 B	"	"	50 min	"
2496 A	"	acetone	55 min	Heavy pitting on entire leading edge; scattered holes through coating.
2496 B	"	"	45 min	"
2387 A	"	50% anti-ozonant in acetone solution	190 min	Coating softened and swelled.
2387 B	"	"	180 min	"
2523 A	"	100% anti-ozonant	220 min	Coating softened and swelled; scattered bubbles formed on high-speed half of leading edge in 120 min and tore open in 220 min.
2520 A	Gaco N-79 neoprene over Bostik 1007 primer (10-12 mils)	none	45 min	Heavy pitting on entire leading edge; scattered holes through coating.
2520 B	"	"	45 min	"

Table 3 (continued)

C.A.L. Spec. No.	Coating System on 2024-0 Aluminum Alloy Airfoils	Treat-ment	Erosion Through Coating	Remarks
2521 A	Gaco N-79 neoprene over Bostik 1007 primer (10-12 mils)	acetone	40 min	Heavy pitting on entire leading edge; scattered holes through coating.
2521 B	"	"	42 min	"
2522 A	"	50% anti-ozonant in acetone solution	105 min	Coating softened and swelled; several bubbles formed on leading edge in approx. 90 min and tore open 15-25 min later.
2522 B	"	"	115 min	"

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large increase in the test life of the neoprene coatings that was produced by the use of antiozonant may have been due simply to adding an additional film so that there was more material to be worn away. This also cannot be a correct explanation since repeated application of tenacious films of silicone oil had no effect in retarding erosion damage to neoprene coatings. Some other factor must be involved and this factor may be that the antiozonant prevents chemical deterioration of the coatings that would result from ozone or from hydroxyl-ion addition if the antiozonant were not used.

With regard to the use of this antiozonant on radomes, it has been stated that it is questionable whether this treatment would be desirable for neoprene coatings used on radomes since the coating becomes very soft and sticky and that this characteristic would undoubtedly have considerable influence on dirt pickup, outdoor durability and electromagnetic wave transmission. As far as softness is concerned, it was brought out in the preceding discussion that excessive softness is not a factor in the enhanced rain-erosion resistance. The experiments using this antiozonant have only utilized strengths of 50 per cent antiozonant and 100 per cent antiozonant and the solutions were applied only at 5-min intervals. Further rain-erosion test-life experiments should be carried out in which the per cent antiozonant or the frequency of application or both are reduced until the conditions that will produce minimum softness with optimum rain-erosion test life are determined.

If a mechanism of ozone addition is involved in the enhanced test life of the coatings that were treated with antiozonant, then outdoor weathering tests should show increased weathering resistance of coatings that are treated with antiozonant. Outdoor weathering experiments should be carried out in which the frequency of application and/or the percent antiozonant that is applied are varied to determine the minimum of antiozonant that should be used.

4.3 Mechanical Fatigue

If rubber is subjected to repeated stretch-and-release cycles it will eventually crack and rupture. A gradual deteriorlation of the rubber accompanies the repeated stretch-and-release process. The dynamic fatigue life may be defined as the number of stretch-and-release cycles that a rubber will survive before rupture occurs.

Cadwell, Merrill, Sloman, and Yost [18] have shown that (A) the fatigue life under linear vibration is lowest if complete recovery is accomplished between successive stretches of a given magnitude; and (B) where the vibration is between larger stretches than (A) but with the absolute magnitude of the stretch being the same as in (A), the fatigue life is very much longer. If the rubber is vibrated in shear, (A) and (B) are also true. Specimens vibrated between zero and 50 per cent shear had only 1/5 the fatigue life of specimens that were vibrated between 75 and 125 per cent shear although the shear oscillation cycle for both was 50 per cent. They also found that (C) increase in the magnitude of the oscillation stroke decreases the fatigue life, and (D) a hard rubber stock has, in general, a lower fatigue life than a soft stock.

If a waterdrop impinges against a rubber or against a rubber-coated surface the rubber is deformed into a cup-shaped cavity by the compressive load and tensile and shear stresses are set up in it; the surface layers of the rubber in and around the cavity are also stretched by the tensile and shear stresses that are exerted by the radial flow of the water of the drop. See Section 5.1.1. When the compressive load is removed and the radial flow of water reaches maximum dimensions and stops, the rubber begins to retract to its original state. If the rubber has a fast recovery it may reach its original unstressed state before another waterdrop impinges and the cycle is repeated. If this is the case, the rubber would be operating under condition (A) with a minimum fatigue life expectancy. If the rubber has a slow recovery rate it may still be in a radially stretched state around the point of one waterdrop blow at the time that another waterdrop strikes the same spot. Under this condition the rubber would be operating under condition (B) with a longer fatigue life expectancy.

In the light of these concepts the recovery properties of a rubber may have a bearing on its rain-erosion resistance. These concepts can only be applied to the failure mechanism of neoprene if it can be shown that the time for a stretch-and-recover cycle is such and the rain density and collision velocity are such that two or more consecutive collisions will occur on the same spot in a time that is equal to or less than the time for a stretch-and-recover cycle. The percent of the collisions

that occur in various time intervals can be calculated if the average drop size of the artificial rain that is used for the tests is known. There is some evidence that the drop diameter of the 1-in./hr artificial rain that is used for the erosion tests at the Cornell Aeronautical Laboratory may be as low as 0.75 mm.

If the drop diameter is taken to be 0.75 mm the volume of a spherical drop is 7.801×10^{-9} cu ft. A rain density of 1 in./hr is then equivalent to 2,967 of these drops per sq ft per sec. If the terminal velocity of the rain is 21.6 ft/sec, then 137.4 of these drops exist in a cubic foot of space. A surface area of one square foot moving at a velocity of 500 mi/hr (735 ft/sec) will sweep through 735 cu ft of air each second or through 101,000 of these drops each second. If it is assumed that the radial flow of each drop that impinges affects a 1/4-in. square , then on the surface area of one square foot that is moving at 500 mi/hr there are 43.8 blows per 1/4-in. square per second.

The probability that a waterdrop blow will occur on a 1/4-in. square in a specified interval of time can be calculated. Assume that (1) the probability of one blow in a time interval Δt is $\lambda \Delta t$ where λ is the average number of blows on the 1/4-in. square per unit time, (2) the chance that a blow will occur in different time intervals is independent, and (3) the probability that two or more blows will occur in the time interval Δt is at least an order of magnitude lower than the probability of one blow. From these assumptions it can be shown [19] that

$$P(X = x) = e^{-\lambda t} \quad (\lambda t)^x \quad / \quad x! \qquad x = 0,1,2\ldots$$

The probability that no blow will occur in a time t is

$$P(X = 0) = e^{-\lambda t}$$

and the probability that one blow will occur in the time interval Δt is $\lambda \Delta t$ by assumption (1). Therefore, the probability that a blow will occur in the time

$t + \Delta t$ is $e^{-\lambda t} \lambda \Delta t$, or in the limit,

$$f(t)dt = e^{-\lambda t} \lambda dt \quad .$$

The probability that a blow will occur in any time interval n is the area A under the curve from $t = 0$ to $t = n$,

$$A = \int_0^n f(t)dt = \int_0^n e^{-\lambda t} \lambda dt = -e^{-\lambda t} \Big|_0^n$$

For a drop diameter of 0.75 mm. λ was found in the preceding calculation to be 43.8 blows per 1/4-in. square per second. For time intervals n of 5 millisec and 3 millisec, the area under the curve is 0.20 and 0.12, respectively. Hence 20 per cent of the waterdrop blows that occur each second on each 1/4-in. square of the surface considered may be separated by a time interval of 5 millisec or less and 12 per cent of these blows may be separated by a time interval of 3 millisec or less. These times are of the order of magnitude to be expected for a stretch-and-recover cycle produced by a waterdrop blow.

In view of the result obtained, the concept that the rate of recovery of a rubber may affect its fatigue life under high-speed rain impingement appears to be feasible. To ascertain whether there is a direct correlation between fatigue strength and rain erosion test life, the fatigue strength and rain erosion test life of neoprene coatings of different properties should be determined. The evidence that has been reported [20] that ozone plays a role in repeated flexing tests suggests that it may be hard to differentiate between the ozone attaction mechanism and the fatigue mechanism; indeed, the fatigue failure may be the result of ozone attack.

5. Mechanism of Rain Erosion of Neoprene Coatings

A large number of experimental observations has been presented in the preceding sections, but more experimental

data are needed for a complete understanding of the mechanism of rain erosion of neoprene coatings. In the remaining sections an effort will be made to analyze and interpret the data that do exist.

5.1 Waterdrop Impingement Stresses and the Response of Structural Materials

The erosion damage that is done to structural materials in high-speed collisions with waterdrops depends both on the properties of a waterdrop in collisions of very short duration and on the properties of the structural material itself.

5.1.1 Stresses

At any given collision velocity the properties of the waterdrop are always the same. In high-speed collisions with a solid surface it acts as though it were a hard solid sphere, but, unlike a sphere of hard solid material, it undergoes an ultrarapid radial flow about the central point of impingement. When a waterdrop collides with the planar surface of a solid, or when the planar surface of a solid runs into a stationary waterdrop, the impact pressure that results reaches a high value in a very short period of time. This high pressure drives the liquid that is close to the solid surface radially outward around the central stagnation point.

The radially flowing liquid exerts a shear stress on the surface of the solid over which it is running. There is a shear stress between the separate layers of the flowing liquid itself and the situation should not be different at the interface between the liquid and a solid surface over which it is moving. The shear stress τ between layers of liquid in laminar flow is given by the product of the viscosity μ and the velocity gradient through the moving sheet of liquid perpendicular to its direction of flow. That is, $\tau = \mu(\partial v/\partial z)$ where v is the velocity of the moving sheet of liquid and z is the direction through the thickness of the liquid sheet. The layer of liquid molecules in direct contact with the solid has zero velocity, but the velocity gradient is not zero and the shear stress is applied to the solid.

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When the liquid from a drop that is flowing radially runs over a surface protrusion it exerts forces against the protrusion that are opposed by the restraint of the bonding of the protrusion to the underlying layers of material. Pressure, σ_p of Figure 27, is exerted against the protrusion by the flowing liquid. The pressure that is exerted by the liquid tends to move the protrusion along the planar surface of the solid and results in a shear stress, τ' of Figure 27, at the base of the protrusion. The flow of the liquid results in the shear stress τ that was discussed above.

The pressure exerted by the liquid also results in a turning moment that tends to bend the protrusion over. The turning moment is the integrated cross product of the compressive force exerted by the liquid and the elevation of the protrusion above the planar surface of the solid at the point where the force is applied. As the protrusion bends, a tensile stress, σ_t of Figure 27, appears on the side of the protrusion against which the compressive force is applied and a compressive stress, σ_p of Figure 27, appears on the opposite side of the protrusion. If the force exerted by the rapidly running liquid is sufficiently great or if the protrusion has a sufficient elevation above the planar surface, failure may occur. Whether the protrusion is simply bent over, whether it is broken off, or whether part of the solid material below the surface is torn out with it depends on the strength of the material and on where failure occurs first. Likely points of failure are marked with notches in Figure 27.

If a waterdrop impinges against a rubber-like material the effect of the compressive stress, σ_p of Figure 28, which is the direct result of the collision, is to compress the solid material at the point of impingement. The local compression results in a dimple or cup-shaped cavity. Tensile stresses, σ_t of Figure 28, appear in the sides of the dimple and especially in the knee in the solid material at the rim of the dimple. If these tensile stresses are sufficiently great tears may form in the surface layers of the solid material. The material that formerly occupied the volume that now forms the hollow of the dimple is displaced. It is moved radially outward and upward around the dimple and this results in a shear stress, τ' of Figure 28.

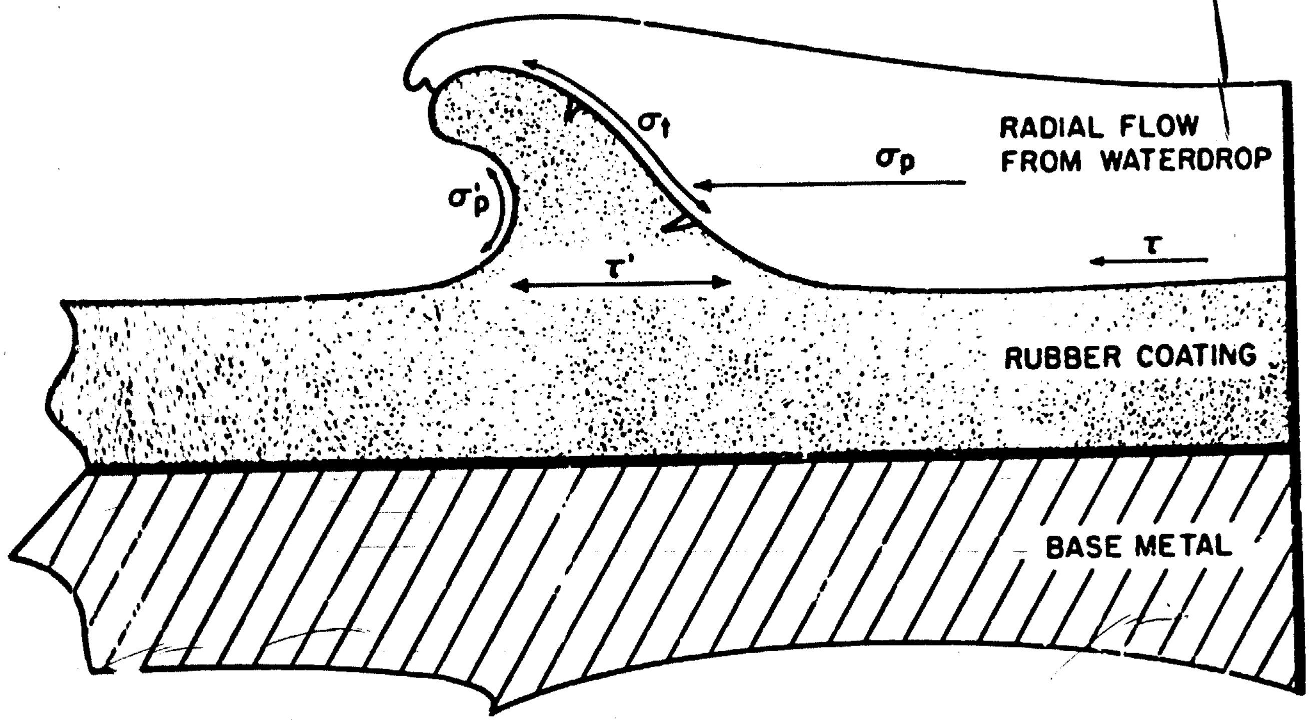

FIGURE 27 STRESSES THAT RESULT WHEN A WATERDROP RUNS OVER A SURFACE PROTRUSION

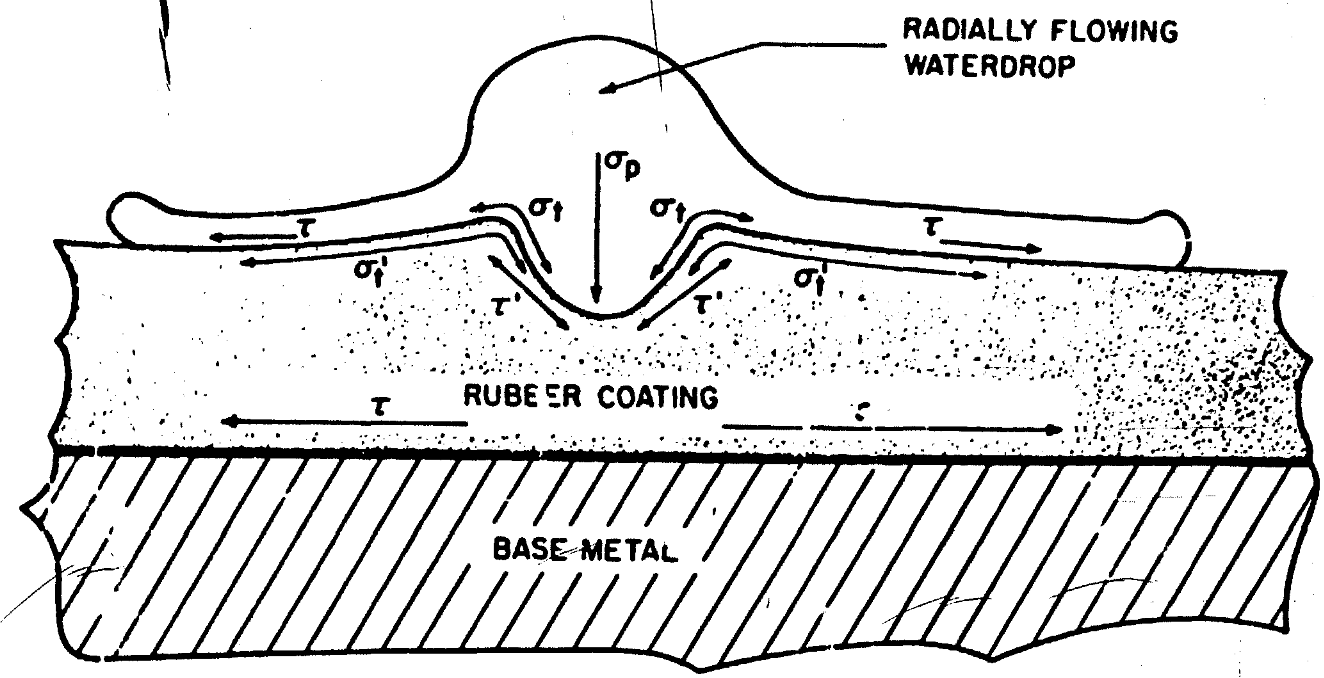

FIGURE 28 STRESSES THAT RESULT FROM THE COLLISION OF A WATERDROP WITH A RUBBER-COATED SURFACE

The radial flow of the liquid of the drop imposes a radial tensile stress, σ_t of Figure 28, and a shear stress τ, which was discussed above. In the case of very thin rubbery coatings it is possible that the shear stress τ may be transmitted through the coating to the primer bonds, which hold the coating to the base metal, and that it may cause failure of the primer-to-rubber or of the primer-to-metal bond. See pictures 2(c) and 3(c) of Figure 10 and the discussion relating to these pictures.

5.1.2 Response of Materials

The damaging properties of an impinging liquid drop that have been considered in the preceding paragraphs are similar ~~for drops~~ of all liquids but vary in intensity depending on the density of the liquid of the drop, on the relative collision velocity, and on the extent to which the solid material yields under the blow. If the characteristic properties of all structural materials were the same, the appearance of damage marks produced by the impingement of drops of a given liquid against all of them at some arbitrary velocity would also be the same; there would be only one type of damage and only one mechanism by which the damage is produced. Because the characteristic properties of structural materials are different there are as many different damage processes as there are broad groups of material properties. A specific question that was posed at the time that the research program on the mechanism of high-speed rain erosion was initiated was whether a soft rubbery material or a hard rigid material should be sought as a solution to the problem. These two extreme cases are considered in the following paragraphs.

A material that behaves like rubber under the blow that results from collision with a liquid drop has the advantage of being a pressure reducer for the blow. When the impact pressure that results from collision with a liquid drop is reduced, the velocity of the radial flow of the liquid of the drop, which is driven by the impact pressure, is also reduced. Because the radial flow velocity is reduced, the shear stress that it exerts, which goes qualitatively as the radial flow velocity, is likewise reduced. The material is, however, depressed at the point where the liquid drop struck and radial tensile stresses appear in the sides of the cup-shaped depression and around, and especially over, the rim of it as it forms. The surface layers of the material are

also stretched around the restricted area of contact between the drop and the surface of the solid as a result of the rapid flow of liquid from the drop. A material of this kind need only have strength properties sufficient to withstand the mitigated stresses in order to be able to remain undamaged on colliding with a liquid drop.

Increase in the indentation hardness of a rubber is commonly accompanied by a decrease in its elongation under a given stress and, therefore, by a decrease in its ability to mitigate the stresses that are imposed on it by high-speed collision with a waterdrop. The indentation hardness associated with maximum resistance against waterdrop-impingement damage at an arbitrary collision velocity is that hardness above which the gain in strength that accompanies further hardening is unable to offset the loss in ability to mitigate the stresses that are imposed by collision with a waterdrop at the velocity in question. In terms of the rupture energy per unit volume the optimum indentation hardness is that hardness above which the area under the stress-strain curve begins to decrease.

All materials yield to some extent under a collision blow. However, materials that do not display a high elongation under a given stress as a result of collision with a liquid drop do not mitigate to a notable degree the stresses that the colliding drop exerts. To be erosion resistant, materials of this class must be able to withstand the unmitigated stresses. Whether or not they can withstand the unmitigated stresses depends on whether they can absorb the energy of the collision blow before their yield or fracture strength is exceeded.

The question that was posed several years ago as to whether the solution to the high-speed rain-erosion problem should be sought among the soft rubbery materials or among the hard rigid materials can be answered in the following way. The material may be hard and rigid or it may be soft and rubbery and still have a high degree of rain-erosion resistance. If it is hard and rigid it must have strength properties that will enable it to withstand without fracture and without plastic flow the maximum unmitigated stresses imposed by collision with a waterdrop in the velocity range for which the material is being tested; these stresses increase in magnitude as the impingement

velocity is increased. If it is soft and rubbery it need only have strength properties sufficient to withstand the mitigated stresses that are imposed by collision with a waterdrop. The velocity ceiling for the rubbery materials is the point at which they are no longer able to withstand the mitigated stresses.

These remarks apply to the ability of a material to withstand a single waterdrop blow. Under actual flight conditions successive blows on the same spot have a certain probability of being very closely spaced in time. Therefore, under flight conditions a rain-erosion resistant rubbery material must not only have strength properties adequate to withstand the mitigated stresses but must also recover fast enough to be able to mitigate the stresses of an additional blow to the extent that they do not exceed its strength properties. To be a practical rain-erosion resistant material the rubber must, furthermore, not lose its ability to mitigate the stresses through deterioration of any kind during its expected service life.

5.2 Failure of the Substrate-Primer-Coating Assembly

A coating may be a simple structure like a paint that bonds naturally to the substrate to which it is applied. Coatings that do not bond naturally to the substrate require a primer that does bond both to the substrate and to the coating. Sometimes a tie-cement is necessary in addition to the primer.

The unqualified use of the expression "rain-erosion resistance" may be confusing when it is applied to coatings that require primers and tie-cements. The rain-erosion resistance of the coating itself is a characteristic of the intrinsic properties of the material of which the coating is composed. The rain-erosion resistance of the coating should not be confused with the rain-erosion resistance of the substrate-primer-coating assembly. If a highly resistant neoprene coating is assembled with a weak primer and/or substrate material the assembly will fail prematurely, but this has nothing to do with the inherent rain-erosion resistance of the coating. Conversely, the rain-erosion resistance of the substrate-primer-coating assembly is improved when a substrate and/or primer of greater strength is used, but the rain-erosion resistance of the coating is not improved. Breakdown of the term rain-erosion resistance

into rain-erosion resistance of the coating and percentage performance or rain-erosion resistance of the substrate-primer-coating assembly is, therefore, desirable.

5.2.1 Loss of Adhesion Due to the Compressive Stress

It was brought out in Section 5.1.1 that if a waterdrop impinges against a rubber-like material the effect of the compressive stress σ_p of Figure 28, which is the direct result of the collision, is to compress the solid material over the area of impingement of the drop itself. The wave of compression that moves through the coating as a result of the collision eventually reaches the primer. The compressional wave is partially transmitted into the primer and partially reflected from it. The reflected portion of the compressional wave is a tension wave that moves back to the surface of the rubber coating. The transmitted portion of the compressional wave moves through the primer and eventually reaches the substrate. Reflection and transmission occur again at the interface between the primer and substrate.

If the primer cannot stand the compression to which it is subjected as the transmitted portion of the compressional wave passes through it, it may fracture or pulverize. Similarly, if the substrate cannot stand the compression to which it is subjected as the transmitted portion of the compressional wave passes through it, it may fracture or pulverize. If either the primer or the substrate pulverize, the adhesion bond between the coating and the substrate may be broken over the area where pulverization occurs. The result of this may be the formation of a dome or bubble of the coating material. The end result, that is, the fact that the coating rises in a dome over the area where the adhesion bond is broken strongly suggests that permanent set may be introduced into it. The unsupported dome of coating material is rapidly broken open when it is struck by additional impinging waterdrops. The coating material that made up the unsupported dome is torn away. The edge of the torn-out area is then subject to being lifted by the radial flow of additional impinging drops; if this occurs the coating may be stripped back further around the area where the original adhesion failure occurred.

It is noteworthy that this type of failure is essentially unrelated to the intrinsic rain-erosion resistance of the neoprene coating itself. Adhesion failure may occur under a very durable neoprene coating and lead to its

early failure. With regard to this type of failure it has been found that use of epoxy glass fabric laminates rather than of polyester glass fabric laminates increases the test life of a given neoprene coating. Application of the neoprene coating to an epoxy laminate for test does not improve the rain-erosion resistance of the neoprene coating but it allows a larger percentage of the intrinsic rain-erosion resistance of the coating to be brought into use.

5.2.2 Loss of Adhesion Due to Shear Stress

Picture 3(c) of Figure 10 provides evidence that adhesion failure may occur without pulverization of the primer or substrate. In the damage mark that is shown in this picture the primer over the central area of the collision that was under compression has remained intact (maximum compression occurs in a ring around this area). Picture 2(c) of Figure 10 provides evidence that the rubber coating is given a drastic radial stretch as a result of the flow of water from the drop. From Pictures 2(c) and 3(c) of Figure 10 it appears that the shear stress τ of Figure 28 is transmitted through the coating and that it causes a shear failure of the primer itself and/or of the primer-to-rubber and primer-to-metal adhesion bonds. It is possible that this type of failure may also occur to a less drastic extent at lower velocities. It is noteworthy that use of a stronger substrate material such as epoxy laminates rather than polyester laminates would have no effect in preventing this type of failure if the failure occurs in the primer or in the primer-to-rubber or primer-to-substrate bonds; it would have an effect if shear failure occurs in the surface layers of the substrate itself. This kind of failure would also lead to the formation of coating bubbles or domes with consequent drastic failure of the coating assembly, that is, with consequent low percentage performance of the coating assembly.

5.3 Failure ~~of the~~ Neoprene Coating

Some of the aspects of the failure of neoprene coatings are a result of, or are enhanced by, the test conditions that are used in their evaluation; others are inherent in the neoprene coatings themselves.

5.3.1 Failure Induced by the Test Conditions

The gradual production of a chevron pattern of grooves in the neoprene at the low-speed end of the specimen seems to be due to the use of tap water for the artificial rain in the rotating arm test. Use of water that was softened to a hardness of less than 2 ppm retarded but did not prevent the appearance of this water-flow pattern in the neoprene. It appears that collision with the tap water rain drops at velocities as high as 500 mi/hr results in precipitation of mineral salts in the water. The conditions is worsened when the collision velocity is increased to 600 mi/hr. The drag of the ~~crystalline~~ precipitate over the surface of the neoprene wears channels along the main trajectories of the flow. Such abrasive wear reduces the thickness of the neoprene coating and may lead to the adhesion failure that results in formation of a dome or bubble of coating and to drastic failure of the coating assembly.

The scouring action of the precipitate-laden water may also be responsible for the removal of the glossy surface layer that originally exists on a neoprene coating. After the surface gloss is removed the intercepted drops strike a dull roughened surface that is more susceptible to the erosion attack.

Modes of failure that can be traced to the abrasive wear of precipitate-laden water are spurious as far as high-speed rain erosion per se is concerned. They should not be considered in arriving at the rain-erosion failure mechanism. They undoubtedly contribute to the deviation of the rotating-arm test results from the results that are found under service conditions. The reliability of the rotating-arm test would be improved if distilled water were used for the artificial rain.

Crack formation in neoprene coatings is to a large extent perpendicular to a line down the leading edge of the specimen, that is, perpendicular to the direction of the strong centrifugal force that exists while the specimen is being whirled on the propeller blade. Ozone cracking does not occur unless the rubber in question is under stress in the presence of ozone; the cracks form

perpendicular to the applied stress. In the case of application of biaxial stress, alligatoring occurs. It is possible that crack formation perpendicular to a line down the leading edge is fostered by the centrifugal force that acts in the rotating arm test. If this is the case, it is spurious as far as true rain-erosion failure is concerned. The undesirable feature of the centrifugal force is inherent in the rotating arm test.

5.3.2 Failure of the Neoprene Coating as a Result of Waterdrop Impingement

Three possible mechanisms of failure of the neoprene topcoat were discussed in Section 4. It remains to evaluate these mechanisms in the light of the experimental data that exist.

5.3.2.1 Abrasion

Some abrasion certainly occurs initially on the surface of neoprene coatings that are tested on the rotating arm. The surface gloss is removed and eventually a chevron pattern forms that marks the trajectories of the water flow off the airfoil shaped specimens. It was pointed out in the preceding section that both these effects may be due to the scraping of the crystalline precipitate in the water. Even when the water was softened to a hardness less than 2 ppm, evidence of cementitious deposit could still be seen on the specimens and the chevron pattern still made its appearance. It is not known whether these evidences of abrasion would disappear if all sources of contamination were removed from the test cell and if distilled water were used for the artificial rain. However, treatment of neoprene coatings with oil, graphite, and detergent in an effort to cut down the coefficient of friction between the neoprene and the flowing water had no effect on the test life of the specimens. Strong reduction of the surface tension of the water that was used for the artificial rain also was without effect. The abrasion mechanism depends on the ability of the flowing water to grip the rubber; these treatments of the neoprene should have affected this ability; since the test life of the specimens was unaffected by these treatments it would seem that abrasion due to the flow of grit-free water is not

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the mechanism by which neoprene coatings fail or that it is not an important mechanism if it makes a contribution to the damage at all.

5.3.2.2 Ozone-type Cracking

Some supporting evidence seems to point to the conclusion that neoprene coatings fail under waterdrop impingement because they suffer chemical deterioration either by addition of ozone or by addition of hydroxyl ions. Ozone is present in the air, and it was demonstrated from theoretical considerations in Section 4.2 that formation of hydroxyl ions can be expected in high-speed collisions of solids with waterdrops. Both ozone and hydroxyl ions are able to add across the double bonds of unsaturated elastomers to produce ozone-type cracking if the elastomer is under stress.

The neoprene coatings are stressed during rain-erosion test not only by the centrifugal force that is applied as a result of the use of a rotating arm but also by the impinging drops. Tensile and shear stresses exist in the rubber when a dimple or cup-shaped cavity forms in it as a result of the local compression caused by a waterdrop collision. Tensile and shear stresses also exist in the rubber as a result of the radial stretch that is given to its surface layer by the flow of the impinging drops. See Section 5.1.1 The conditions for ozone-type crack formation are, therefore, present during high-speed waterdrop impingement against neoprene coatings.

Crack formation that strongly resembles ozone-type cracking in biaxially stressed rubber (alligatoring) have been observed in eroded neoprene coatings. These cracks were not observed in eroded neoprene coated specimens that had been treated with antiozonant during rain-erosion test. Use of an antiozonant appears, therefore, to prevent the cracking.

Use of the antiozonant did soften the neoprene coatings, but to ascribe the enhanced rain-erosion resistance of antiozonant-treated neoprene coatings to softening is out of keeping with the test observation [17] that high rain-erosion resistance is associated with high Durometer

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hardness. The antiozonant is applied to the coatings externally but to ascribe the enhanced rain-erosion resistance of the antiozonant-treated neoprene coatings to addition of an extra layer that must be worn through is out of keeping with the test result that application of tenacious oil films had no effect on the rain-erosion test life of neoprene coatings.

The rain-erosion of neoprene coatings is a two-step process consisting of periods of preparation in which little loss of material occurs followed by periods of erosion or loss of material. This is clearly shown in the graphs of Figure 23 and 25. The gradual development of a network of ozone-type cracks with eventual breaking away of material between circumscribing cracks is such a two-step process.

A question that may be raised is why the rain-erosion failure of neoprene coatings is more drastic at a test velocity of 500 mi/hr than at a test velocity of 600 mi/hr if the failure mechanism is a chemical deterioration. With regard to the addition of ozone, the concentration of ozone naturally present in the air would be the same regardless of the test velocity. However, a strong possibility exists that fewer waterdrops actually impinge on the leading edge of the rotating arm at a test velocity of 600 mi/hr than at a test velocity of 500 mi/hr. If this is the case, the rubber sustains fewer local stresses at the higher velocity and it requires both ozone and stress to produce ozone cracking. With regard to the addition of hydroxyl ion, the formation of hydroxyl ion is fostered at a test velocity of 500 mi/hr because the acid carbonate ion in the water withdraws hydrogen ion from the equilibrium to form poorly ionized carbonic acid.

$$
\begin{array}{ccccc}
2\,H_2O & \rightleftharpoons & 2\,H^+ & + & 2\,OH^- \\
 & & + & & \\
Ca(HCO_3)_2 & \rightleftharpoons & 2\,HCO_3^- & + & Ca^{++} \\
 & & \big\downarrow\!\uparrow & & \\
 & & H_2CO_3 & &
\end{array}
$$

When the test velocity is increased to 600 mi/hr calcium carbonate precipitates to a more marked degree. The acid carbonate ion is withdrawn from the equilibrium to form calcium carbonate precipitate and the formation of hydroxyl ion is no longer favored. In terms of this explanation there

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3\downarrow + CO_2\uparrow + H_2O$$

is less hydroxyl ion present to attack the rubber at a test velocity of 600 mi/hr than at a test velocity of 500 mi/hr.

The experimental evidence that has accumulated is by no means exhaustive but the evidence that has been cited supports the mechanism of deterioration by addition of ozone or of hydroxyl ion as being a means by which neoprene coatings may fail under high-speed rain impingement.

5.3.2.3 Effect of Rate of Recovery on Fatigue Life

Rate of recovery may have some effect on the test life of neoprene coatings but no experimental data exist at present to prove or disprove it. To determine whether or not rate of recovery contributes to the test life of neoprene coatings specimens should be coated with neoprenes having different recovery rates. These specimens should all be treated with antiozonant to prevent ozone-type cracking from playing a role. The test life of the specimens should then be compared. These data are not now available and this point for the present will have to remain unanswered.

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Unclassified report

The mechanism by which neoprene coatings fail is of interest becuase air traffic will be carried on for many years to come in the altitude range in which rain is still encountered and in the velocity range for which neoprene coatings are a solution to the rain-erosion problem. This report is

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